

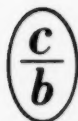
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ERRATA

The following illegibilities appear in this text, as a result of mechanical reproduction difficulties. These difficulties have been eliminated, and subsequent issues will be completely legible.

Illegible portion reads

- Page 72... The alcohol was distilled off, the residue diluted with water and treated with ether. Fractionation of the reaction products yielded 14.5 g. 1-butoxy-2,4-pentadiene, and 8 g. of a fraction, boiling in the range 117-135°C (16 mm), which on repeated fractionation yielded 6.2 g. 1-5-dibutoxy-3-pentene.
- 116... 2) Di-(o-methoxy)-phenyl ester of phosphorosomonochloride.
... 0.2410 g.
... After standing at room temperature for 3-4 hours or heating for 30 minutes at 40-50°C the reaction mixture is poured into five times its volume of cold water. The oil separating out initially slowly crystallizes upon standing. It is filtered off, washed with a 5% solution of HCl, then carefully with water, dried and recrystallized from a suitable solvent.
- 136... Methosulfatemetethylate-o-methylisothebaine
... Methosulfatemetethylate of inactive des-base
... Trimethoxyphenanthrene picrate
- 146... In the formic acid-formic ethyl ester and formic acid-ethyl ether systems (Figs. 3 and 4) all isoconcentrates of the diagrams of molecular weight...
- 147... 0.8547
- 166... The formation of o-lactyl-phenyl-glyoxylic acid (IV) is not only due to the hydrolyzing action of the medium. As will be shown in a subsequent communication [4], 2-methyl-1,4-naphthoquinone oxide...
... derivatives with sodium bisulfite and no corresponding derivatives with p-nitrophenylhydrazine and semicarbazine. The acid (IV) was fairly resistant to hydrolytic cleavage; it was practically unchanged on prolonged boiling with 1% aqueous sulfuric acid, and also in an aqueous buffer solution at pH = 7.2. However, at a higher pH value, it may undergo changes (see below). Thus, the preliminary investigation established definitely only the presence of one carboxyl group in the molecule. The presence of carbonyl and hydroxyl groups could not be confirmed, although the 5 oxygen atoms and a positive reaction with ammoniacal silver suggested their presence.
- 170... from the system was continued for 3 hours, the water in the reaction flask being boiled to remove any traces of dissolved air. The vessel with the oxide sample was immersed in boiling water and the boiling continued for 24 hours while continuously passing through a current of hydrogen. The separation of the reaction products and their purification were carried out under the conditions described in experiment 1a. Yield: 0.25 g. 2-methyl-1,4-naphthoquinone, 2.3 g. phthiocol, and 0.4 g. p-lactyl-phenyl-glyoxylic acid.

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ATOMIC WEIGHT AS A PERIODIC FUNCTION:

A STUDY OF BINARY ELEMENTS¹

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When the periodic law was first formulated, the element weight², as is known, served as a foundation; although in doubtful cases, D. I. Mendeleev used another characteristic -- the atomic number -- to establish the sequence in his system. In the beginning of the twentieth century the atomic number, experimentally determined by measurement of the charge on the atomic nucleus, was taken as the basis for the periodic law. Since that time the element weight has been usually considered as a special unperiodic, discontinuous function of the atomic number, the latter characterizing the position of the elements in the system.

Considering this function graphically (on the abscissa -- the atomic number, on the ordinate -- the element weight), we observe that the discontinuous functions, i.e. the difference in weight of neighboring elements, are quite variable in magnitude. These differences can be conditionally distributed into 5 classes:

- 1, ΔE in 5 cases are negative and vary from -1.12 to -0.25;
- 2) ΔE is positive and varies about 1 (in the limits from 0.79 to 1.323); such differences are observed in 19 cases;
- 3) ΔE is positive and varies about 2, i.e. in the limits from 1.56 to 2.48; 26 of such cases;
- 4) ΔE is positive and varies about 3 (in the limits from 2.65 to 3.43); 25 of such cases;
- 5) ΔE is positive and higher than 3, varying about 4 (in the limits from 3.64 to 4.487) in 12 cases, about 5 (from 4.53 to 5.12, in 5 cases, and finally, in one case equals 5.85, in another 7.07, and in still another case even reaches 11.

The principal concentration of these differences (rounded off to one figure after the decimal point) is situated around three basic numbers, in the proximity of 1, 2 and 3 as is shown in Figure 2.

Presented January 9, 1947. at the science session of the L.O.L.G.U.

² The term "element weight" was proposed by D. I. Mendeleev, but did not receive wide circulation during his lifetime, and is only now beginning to be used instead of the previously inconvenient (since the discovery of isotopes) expression "atomic weight".

Let us look in somewhat greater detail at the aforementioned 5 classes.

1) Negative values of ΔE are observed for the pairs of elements indicated in Table 1.

The three first pairs were known even by Mendeleev as special, so-called anomalous element weights.

2) At the end of the last century Lorentz¹⁾ developed the idea that the neighboring elements in the table originated, like twins, in pairs since the components of each pair showed little difference from each other in element weight. He considered as twins all those pairs of elements whose difference of element weight did not exceed the absolute figure of 1.4.

Therefore, the pairs we considered to be in the first and second classes would, according to Lorentz, be twins.

D. I. Mendeleev, in "Fundamentals of Chemistry" ²⁾ wrote, in this connection: "a similar relationship exists among many elements close to each other in atomic weight, which has been observed for some time (the first edition of the "Fundamentals" was published in 1869), and probably possesses some connection, not clear at the present time, with the mutual relationships of the elements and the periodic law.... in my opinion the above relationship can only be explained in conjunction with the periodic system".

Therefore we see that D. I. Mendeleev considered significant the study of pairs of elements, or according to his terminology, binaries.

Let us list the binaries of the second class. The ones known to Lorentz are marked with an asterisk, and we place in parentheses those which, according to the considerations developed below, are not considered actual binaries, although they are close to each other in weight. (See Table 2)

If, following the Aston rule of isotopes, we assume the weight of Ru to be 101.1 and not 101.7, then the difference for Ru-Rh will be equal to 1.8 and is relegated to the third class.

D. I. Mendeleev also turned his attention to the concept that the lightest elements, components of one or another binary, are either perissads¹ or artiads¹, and observed that "The above-described rule is of significance in the study of the elements". The author of the present paper has found that in the beginning of the System (to Ga³²) binaries of only one type are encountered, i.e. -- "perissad - artiad" (8 cases); after gallium, on the other hand, binaries of the opposite type are found, i.e. -- "artiad - perissad" (also 8 cases). The elements in brackets, La - Ce, Bi - Po, and Am - Cm at first glance contradict the second of these types, but actually these elements are not binaries. Actually, Ce forms a binary with Fr but not with La, since the latter produces a binary with Ba (Table 3); the difference of Ba-La being equal to 1.56, which is only slightly higher than the maximum limit we arbitrarily placed of 1.323 and Lorentz' maximum of 1.4; the difference in mass of the principal isotopes, ¹³⁹La - ¹³⁸Ba being equal to 1. Similarly, Po forms a binary with At, but not with Bi, which actually forms a binary with Pb (Table 3), wherein the Pb-Bi difference equals 1.79; the difference in mass of the principal isotopes ²⁰⁹Pb - ²⁰⁸Pb being equal to 1; americium forms a binary with plutonium, wherein the Pu - Am difference equals 2 (Table 3); Cm is paired with an element, thus far unknown, transcurium No. 97.

¹ Perissad is the Greek for "odd-numbered", i.e. elements with an odd atomic number and most often with odd-numbered weights and valencies. Artiad is the Greek for "even-numbered".

It is clear from the above that the term "binary" as used by the author connotes those neighboring elements whose difference in weights is noticeably greater than 1.

It is clear that for all 19 cases shown in Table 2, concerning differences of the second class, the increase of element weight is accomplished chiefly by another proton appearing in the nucleus, and the average increase of the number of neutrons approaches zero. Therefore, these differences can be characterized as pertaining to the approximately isoneutron elements. On Figure 1 it is seen that the binaries lie close to the isoneutrons, the number of which we have shown in the last column of Table 2. Thus, the isoneutron No. 82 (corresponding to atoms with that number of neutrons in the nucleus, that is, 82) is represented by the straight line $O''A''$, and No. 126 by the straight line $O'''A'''$. The isoneutron triads La - Ce - Pr and Bi - Po - At lie on the isoneutrons No. 82 and No. 126. It is characteristic that all the isoneutron numbers of our table are even.

3) The following differences (Table 3) belong to the third class.

It is evident from the table that, beginning with Ge^{32} , the binaries marked with an asterisk belong to the arliad - perissad type.

Increasing the element weight by 2 results in an increase of 1 proton and 1 neutron, i.e. in these cases there is a constant difference between the number of neutrons N and the number of protons P or $\Delta(N-P) = 0$. It is evident that those discontinuous functions of interest to us will parallel the sharply rising straight line OB (Figure 1), or an isodifference of 0 (the line indicating the $N-P$ difference of 0). The triad C - N - O lies approximately on the line OB, since the difference between the number of neutrons and the number of protons in the nuclei of the principal isotopes of these elements is equal to zero. The triad Li - Be - B corresponds to the isodifference No. 1. Two triads: Kr - Rb - Sr and Yt - Zr - Nb, are close to the isodifference No. 11; the tetrad Dy - Ho - Er - Tm corresponds to the isodifference no 31, the triad Ir - Pt - Au to the isodifference No. 39, and, finally, the triad Np - Pu - Am to the isodifference No. 51. The remaining 12 approximately isodifferential pairs are independent, i.e., do not fall into the categories of triads or tetrads.

We see, then, that according to our interpretation, out of the 26 isodifferential pairs, 12 (marked in Table 3 with asterisks) must be considered as binaries, since the principal isotopes differ in mass by 1 from their isoneutrons. This difference results from the action of secondary isotopes on the element weight. We name such binaries hidden binaries or binaries with complex isotopic pleiads to distinguish them from the actual binaries examined above.

Also, in Table 3 there are 7 still more camouflaged binaries of a special type, marked with two asterisks. They will be discussed further below.

4) The following differences (Table 4) belong to the fourth class.

Here we observe almost rectilinear portions, consisting of close, successive differences: $H^1 - He^2 - Li^3$; $Sc^{21} - Ti^{22} - V^{23}$; $Nb^{41} - Mo^{42} - Tc^{43} - Ru^{44}$; $Pr^{59} - Nd^{60} - Sm^{61} - Eu^{62}$.

Of course these portions are steeper than the line OB, since they correspond to the increased difference of $N-P$ here $\Delta(N-P)$ is close to 1 (monodifferential portion).

Out of the 25 pairs 3 must be considered as doubtful binaries with complex pleiads, e.g. $Mo^{42} - Tc^{43}$, $Sn^{50} - Sb^{51}$ and $Os^{76} - Ir^{77}$. The difference in mass of their chief isotopes can be expressed by 1, the greater figure for ΔM resulting from the secondary isotopes.

Indeed, the pleiads of these elements are shown in Table 5.

The presence of large quantities of light isotopes $_{92}Mo$, $_{94}Mo$, $_{96}Mo$ lowers the

element weight of molybdenum and increases ΔE . The presence of light ^{116}Sn and ^{118}Sn lowers the element weight of tin, and heavy ^{123}Sb increases the weight of antimony; as a result, ΔE increases from 1 to 3.

The pleiads of osmium and iridium are shown in Table 6.

The light isotopes of osmium ^{188}Os , ^{189}Os and ^{190}Os lower its element weight and increase ΔE .

5) The following differences belong to the fifth class (Table 7).

It is interesting that the greater differences, corresponding to the di-, tri- and megalodifferentials pertain to those pairs of elements in the System principally before and partially after Ar, Kr, X and Ru, and also the lanthanide and actinide series. In the small periods from No. 1 to No. 17, and also in the portions from Sc^{21} to Ni^{28} and from Kr^{36} to Rh^{45} there is no marked transition. This situation is clearly seen from Table 8.

From Table 8 it is evident that in a series of cases, the major mass transfer to chemical analogs seem to be periodically repeated; as, for example, the transfer from halogens to inert gases; the transfer from As and Sb to Se and Te; the transfers from Zn and Hg to Ga and Tl. Of course in a given case, periodicity of the Mendeleev type (i.e. with classical long periods) is not as evident as in the theory of the electronic shells, but the hypothesis can be expressed that this periodicity exists although in camouflaged form. In Figure 1 alternating maxima and minima are not evident, but on the other hand the successive repetition of regions with dense and sparse points, the latter denoting the individual element weights, is quite marked. It can be assumed that periodicity is not evident as alternating maxima and minima, but only appears in several indistinct dense and sparse points arising from the coexistences of at least two functions: one, quickly rising and regular, and the other, periodic, superimposed on the first, starting from the larger periods of the System. As a result, instead of maxima there is obtained only regions of sparse points, corresponding to Ar, Kr, X and Rn.

In the small periods the even element weights, as is known, are approximately double the atomic number, and the odd element weights are greater than double the atomic number, by 1. The even weights, up to calcium, proceed along the isodifferential No. 0, the odd along No. 0. After calcium, the increase of E becomes sharper, but we can see that this growth is a prolonged, gradual, isodifferential rise, which is dependent on the excess of neutrons. The periodicity of which we have spoken is obviously connected with the number of excess neutrons, i.e. with the excess $N - P$ greater than zero, which corresponds to the isodifferential No. 0. The points on Figure 1 become sparser when $N - P$ increases more sharply, and on the other hand, become denser when the difference between the number of neutrons and protons increases more slowly.

In order to make the periodicity more evident in a diagram, it would be advantageous to let the abscissa be P but the ordinate not be P , but $E - 2P$, since this quantity makes it easier to consider and to express the average excess of neutrons over the protons for the isotopic pleiads of a particular element. Figure 3 expresses this relationship of $E - 2P = f(P)$.

In figure 3 certain regions clearly project, corresponding to the inert gases (Ar, Kr, X, Rn); here it is noticed that the tendency toward an increase in excess neutrons is periodically repeated, which is represented by complex maxima on the curve. In the same figure it is seen that the isoneutronic portions impart a serrated appearance to the curve, in which the

true binaries lie immediately on the isoneutrons, but are masked by the complexity of their pleiads surrounding the corresponding isoneutrons. Various types of binaries up to gallium and following it are also evident in the figure. The path of the isodifferential is now shown on the approximately horizontal portion. It is evident that if the equation $E - 2P = f(P)$ is expressed by two equations, individually by the artiad and perissad, the serrated character of the diagram will disappear, the perissad curve up to gallium lying above the artiad curve, and after gallium the reverse. It is clear that at the gallium point, i.e. on the isoneutron No. 38, the curves will intersect. The isoneutronic portions, previously uniting two curves into one, now disappear, but characteristically the isoneutrons No. 82 and No. 126, previously on both curves, are still present. It is observed that the difference of $126 - 82$ and $82 - 38$ are equal to one another.

Thus, besides the Mendeleev periodicity and the artiad-perissad periodicity, we also observe still a third type of repetition in the System, represented by the special isoneutrons Nos. 38, 82 and 126.

The disappearance of the serrations, which takes place upon shifting from two curves to one, is accompanied, of course, by the appearance of horizontal isodifferential portions.

To explain the periodicity we observed we must, of course, shift from the average element weights \bar{E} to the atomic weights A of the subelements, i.e. to the isotopes of the element pleiads. In order to avoid confusion, we will, in the present paper, limit each element to the nuclei most widely distributed in nature, which we will conditionally call the chief subelements.

We observe that in several cases of isotopic pleiads, the type of atom which is clearly predominate over all others is absent. Thus, for example, for bromine we have two isotopes, mixed in the following percentage relationships 50.9 and 49.1; for tellurium there are 8 isotopes with the contents: 33.1, 32.8, 19.0, 6.0, 4.5, 2.9, 1.6 and 0.1. In all such cases we considered the principal isotopes as those which were found distributed in a quantity greater than 0.1%. Further experimental work may, in some cases, change the choice of the chief isotopes, but in any case a diagram is obtained by the present data which is convincing in its simplicity and orderliness.

This relationship of $A - 2P$ for the principal artiad and perissad subelements is interestingly presented in Figure 4.

For simplicity and to avoid consideration of errors in mass, we prefer to represent on Figure 4 not $A - 2P$, but a quantity very close to it in magnitude, $N - P$; i.e. not the difference in mass, but the difference of the total number of neutrons and the number of protons in the corresponding nucleus or "the number of excess neutrons".

Examining the diagram, we see that the perissad curve has a simpler construction than the artiad curve; the principal perissads being situated in a geometric pattern, passing alternately from a horizontal plateau -- becoming more infrequent and shorter toward the end of the system, to a more vertical, coinciding with the $N - P$ rise. Only in three places does a drop occur instead of a rise.

The first of these corresponds to a shift from ${}_{11}\text{B}^5$ to ${}_{14}\text{N}^7$, where the number of excess neutrons falls from 1 to zero. After nitrogen the curve once more returns to the ordinate of 1, but this temporary drop does not affect the course of the curve, being caused only by a specific characteristic of nitrogen, that is, the prevalence of the

isotope $2N$, i.e. perissad nuclei with an even mass and odd charge occur, as is known, in four elements at the beginning of the system.

Even more important is the second (isoneutron) drop -- from $_{83}\text{La}^{87}$ to $_{81}\text{Pr}^{89}$, where the excess of neutrons falls from 25 to 23, this drop continuing in the perissad curve to the end of the system. Analogously, there is an isoneutron drop from $_{83}\text{Bi}^{83}$ to $_{81}\text{At}^{85}$. The inclined segments on the curve for the principal perissads with three exceptions all have the same slope, that is: for each two new protons there are four neutrons, i.e. the number of excess neutrons increases by two units; this corresponds to the increase of the atomic weight by 6 units upon increasing P by 2, or an increase of 3 units upon increasing P by one. The three afore-mentioned exceptions, that is those affecting the slope of the curve, will now be considered.

Two of these are on the transition from $_{47}\text{Ag}^{47}$ to $_{49}\text{In}^{49}$ and from $_{79}\text{Au}^{79}$ to $_{81}\text{Tl}^{81}$. In both cases the increase, steeper than usual, corresponds to an increase in the mass of the principal isotopes not by 6 but by 8 units, i.e. for 2 protons there are not 4 but 6 neutrons: the number of excess neutrons therefore increases not by 2 but by 4 units.

It is characteristic that both increases lie at the chemical analogs -- silver and gold, which again is reminiscent of the Mendeleev periodicity.

The transition from copper to gallium also possesses a specific characteristic, but of another kind -- here a phenomenon takes place which is not repeated in any other part of the system: the intersection of the perissad and artiad curves.

The third of these aforementioned exceptions is the transition from $_{85}\text{At}$ to $_{87}\text{Fr}$; the increase here is especially sharp, the mass increase being equal to 12, i.e. for two protons there are 10 neutrons. The number of excess neutrons is increased to 8.

In connection with the simple structure of the course taken by the principal isotopic perissads we will assume that the perissad curve we have studied is the central stem of the system of elements. This hypothesis, as we shall see later, seems suitable in every case.

The artiad curve of the principal isotopes, in general parallels the perissad curve, with the very substantial exception in one location, where the curves intersect; besides which, in several positions of the system the principal artiads fall either below or above the main path. This is indicated on the diagram (Figure 4) by pointers. After each of these variations, which depend upon the rule of isobars, discovered by us in 1922, the artiad curve returns to its principal path, parallel to the perissad curve. These variations are quite numerous, but still do not alter the evident parallelism of the paths.

As was just mentioned, the single irreversible departure from the parallelism is observed in the transition from $_{64}\text{Zn}^{60}$ to $_{74}\text{Ge}^{72}$, which is so sharp that the artiad curve crosses the perissad curve at a point corresponding to $_{63}\text{Ga}^{63}$. The rise from $_{64}\text{Zn}$ to $_{74}\text{Ge}$, i.e. 10 units at once, corresponds to an increase of 2 protons and 8 neutrons; here the number of excess neutrons increases 6 units. This rise is still sharper than the transition from Ag to In and from Au to Tl.

Since in general the artiad curve parallels the perissad curve, it is self evident that there is a sharp rise on the artiad curve from Pd to Cd and from Pt to Hg, analogous to the rise from Ag to In and from Au to Tl.

At the isoneutron of the perissad La to Pr, there is an analogous drop in the artiad curve from Ba to Ce. As a result in the portion from La to Ce both curves coincide but do

not intersect.

At the second isoneutron of the perissad Bi to At, there is an analogous drop in the artiad curve from Pb to Po. It is easily seen that as a result of the parallelism of the curves, the principal artiad and perissad isotopes, generally speaking, are broken up into binaries or isoneutron pairs, with the exception, of course, of those cases where the isobar artiad deviations complicate the diagram.

Also it is clear that as a result of the intersection of the curves, the pairs before gallium are constructed differently from those after gallium. Gallium itself is not paired.

As can be seen, there are two rules:

1) Up to gallium, the principal artiaids are greater in mass by one over their perissad pairs, with the exception of H, Be, N, Ar, Ti and Ni, where the isobar deviations are evident and special conditions characteristic for the beginning of the system.

Actually we have 9 normal pairs:

${}^1_1\text{H} - {}^2_2\text{He}$, ${}^{19}_9\text{F} - {}^{20}_{10}\text{Ne}$, ${}^{23}_{11}\text{Na} - {}^{24}_{12}\text{Mg}$, ${}^{27}_{13}\text{Al} - {}^{28}_{14}\text{Si}$, ${}^{31}_{15}\text{P} - {}^{32}_{16}\text{S}$,
 ${}^{39}_{19}\text{K} - {}^{40}_{20}\text{Ca}$, ${}^{51}_{25}\text{V} - {}^{52}_{26}\text{Cr}$, ${}^{55}_{27}\text{Mn} - {}^{56}_{28}\text{Fe}$, ${}^{63}_{29}\text{Cu} - {}^{64}_{30}\text{Zn}$.

and 6 pairs, complicated by the artiad deviations:

${}^3_2\text{He} - {}^4_3\text{Li}$	instead of	${}^3_2\text{He} - {}^4_3\text{He}$
${}^7_3\text{Li} - {}^8_4\text{Be}$	" "	${}^7_3\text{Li} - {}^8_4\text{Be}$
${}^{14}_7\text{N} - {}^{16}_8\text{O}$	" "	${}^{15}_7\text{N} - {}^{16}_8\text{O}$
${}^{35}_{17}\text{Cl} - {}^{40}_{18}\text{Ar}$	" "	${}^{35}_{17}\text{Cl} - {}^{36}_{18}\text{Ar}$
${}^{45}_{21}\text{Sc} - {}^{48}_{22}\text{Ti}$	" "	${}^{45}_{21}\text{Sc} - {}^{46}_{22}\text{Ti}$
${}^{59}_{27}\text{Co} - {}^{58}_{28}\text{Ni}$	" "	${}^{59}_{27}\text{Co} - {}^{60}_{28}\text{Ni}$

2) Following gallium the principal artiad isotopes, on the other hand, are less in mass by one than their perissad pairs, with the exception of Se, Zr, Te, Nd, Er, W, Pt, Hg, where the isobar deviations are present.

Actually, there are 21 normal pairs:

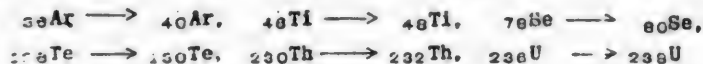
${}^{74}_{32}\text{Ge} - {}^{76}_{33}\text{As}$, ${}^{84}_{36}\text{Kr} - {}^{86}_{37}\text{Rb}$, ${}^{88}_{38}\text{Sr} - {}^{90}_{39}\text{Yt}$, ${}^{98}_{42}\text{Mo} - {}^{100}_{43}\text{TC}$, ${}^{102}_{44}\text{Ru} - {}^{103}_{45}\text{Rh}$, ${}^{106}_{46}\text{Pd} - {}^{107}_{47}\text{Ag}$,
 ${}^{114}_{48}\text{Cd} - {}^{115}_{49}\text{In}$, ${}^{120}_{50}\text{Sn} - {}^{121}_{51}\text{Sb}$, ${}^{132}_{54}\text{X} - {}^{136}_{55}\text{Cs}$, ${}^{138}_{56}\text{Ba} - {}^{139}_{57}\text{La}$, ${}^{140}_{58}\text{Ce} - {}^{141}_{59}\text{Pr}$, ${}^{152}_{60}\text{Sm} - {}^{153}_{61}\text{Eu}$,
 ${}^{158}_{62}\text{Gd} - {}^{159}_{63}\text{Tb}$, ${}^{164}_{64}\text{Dy} - {}^{165}_{65}\text{Ho}$, ${}^{174}_{68}\text{Yb} - {}^{175}_{69}\text{Lu}$, ${}^{180}_{70}\text{Hf} - {}^{181}_{71}\text{Ta}$, ${}^{192}_{74}\text{Os} - {}^{193}_{75}\text{Ir}$,
 ${}^{208}_{82}\text{Pb} - {}^{209}_{83}\text{Bi}$, ${}^{210}_{84}\text{Po} - {}^{211}_{85}\text{At}$, ${}^{222}_{86}\text{Rn} - {}^{223}_{87}\text{Fr}$, ${}^{226}_{88}\text{Ra} - {}^{227}_{89}\text{Ac}$.

and 11 pairs, complicated by the deviations:

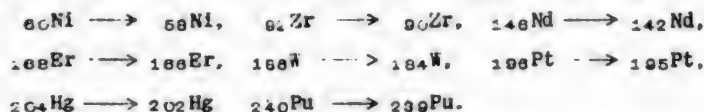
${}^{80}_{34}\text{Se} - {}^{79}_{35}\text{Br}$	instead of	${}^{78}_{34}\text{Se} - {}^{79}_{35}\text{Br}$
${}^{92}_{40}\text{Zr} - {}^{93}_{41}\text{Nb}$	" "	${}^{92}_{40}\text{Zr} - {}^{93}_{41}\text{Nb}$
${}^{130}_{52}\text{Te} - {}^{121}_{53}\text{I}$	" "	${}^{126}_{52}\text{Te} - {}^{127}_{53}\text{I}$
${}^{142}_{60}\text{Nd} - {}^{147}_{61}\text{Pm}$	" "	${}^{146}_{60}\text{Nd} - {}^{147}_{61}\text{Pm}$
${}^{166}_{64}\text{Er} - {}^{169}_{65}\text{Tm}$	" "	${}^{166}_{64}\text{Er} - {}^{169}_{65}\text{Tm}$
${}^{184}_{76}\text{W} - {}^{187}_{77}\text{Re}$	" "	${}^{186}_{76}\text{W} - {}^{187}_{77}\text{Re}$
${}^{196}_{78}\text{Pt} - {}^{197}_{79}\text{Au}$	" "	${}^{196}_{78}\text{Pt} - {}^{197}_{79}\text{Au}$
${}^{204}_{80}\text{Hg} - {}^{205}_{81}\text{Tl}$	" "	${}^{204}_{80}\text{Hg} - {}^{205}_{81}\text{Tl}$
${}^{232}_{90}\text{Th} - {}^{231}_{91}\text{Pa}$	" "	${}^{230}_{90}\text{Th} - {}^{231}_{91}\text{Pa}$
${}^{238}_{92}\text{U} - {}^{237}_{93}\text{Np}$	" "	${}^{236}_{92}\text{U} - {}^{237}_{93}\text{Np}$
${}^{239}_{94}\text{Pu} - {}^{241}_{95}\text{Am}$	" "	${}^{240}_{94}\text{Pu} - {}^{241}_{95}\text{Am}^1$

¹ Element 97, if discovered, would probably form a complex pair with Cm.

Thus, there are 30 normal pairs, the unpaired gallium and 17 deviating pairs. Of these, 3 cases are explained by the special characteristics present in the beginning of the system, and the remaining 14 cases may be explained by the artiad deviations. Of the 14 deviations, 6 deviate upward (i.e. - from the principal path, upward);



and the remaining 8 are characterized by a downward motion, i.e. a decrease in mass:



Further material on these special artiaids and their connection with the anomalies of the element weights (Ar - K, Co - Ni, Te - I, Th - Pa, U - Np) will be discussed in a separate paper.

From Figure 4 it is evident that the system of elements is divided into four parts by the isoneutrons No. 38, No. 82, and No. 126.

1. From the beginning of the system to the element gallium (up to the intersection of the artiad and perissad curves). This region includes the elements most widely distributed in nature.

2. From gallium to lanthanum, in which the artiad and perissad curves, in a small portion, coincide and drop, since the change in mass of the five principal neighboring isotopes is only equal to one:



The lanthanide series begins here.

3. From lanthanum to bismuth, in which the region of stable isotopes ends, the artiad and perissad curves, as in the previous case, coincide and drop, since the principal isotopes of the four elements change in mass successively by one;



4. From bismuth to the end of the system - the region of the radioactive elements.

It is of interest that 69Ga^{31} , 139La^{57} , 209Bi^{83} are characterized by an equal increase in the number of protons and neutrons: the atomic mass of lanthanum is greater than the atomic mass of gallium by 70, this difference corresponding to an increase of 26 protons and 44 neutrons. Bismuth and lanthanum also have a difference of 70, consisting of 26 protons and 44 neutrons. The same difference holds between 138Ba^{56} , and 208Pb^{82} .

On the basis of the material presented, we conclude that the nuclear periodicity is more complex than the periodicity of the electronic shells, and is expressed in at least three manners:

1) in the alternation of the even (artiad) and odd (perissad) elements with their peculiarities;

2) in a periodicity reminiscent of the usual, classical periods of the electronic shells;

3) in the division of the nuclear system into four parts by the isoneutrons No. 38, No. 82, and No. 126.

The first of these three periodicities was discovered by Harkins and recently interestingly developed by Semenchenko and Korobov⁴).

The second was observed by the authors of the present paper in 1922 and published in a form antiquated by present standards.

Further, the conception of periodicity was developed in a new and original manner by I.P. Selinov, who independently developed a neutron proton theory of the nucleus⁵).

The third type of periodicity was observed by the author in 1946.

The complexity of the nuclear periodicity possibly results from the proton-neutron dualism.

On the basis of the material presented, we may propose the following formulation of the Periodic Law of Mendeleev:

"The physical and chemical properties of the elements, dependent upon the electron shells and also the element (atomic) weights are periodic functions of the number of particles composing the shell or the nucleus, i.e. the number of electrons (in the first case) or the number of nucleons (neutrons and protons, where the nucleus is concerned)".

It must be noted that the observation made 80 years ago by D.I. Mendeleev on the probable connection between the existence of binary elements and the "generally mutual relationship of the elements" have been confirmed by our discussions, which have also brought out new ideas arising from the thesis of the parallelism of the principal artiad and perissad paths. Another observation of D.I. Mendeleev on the two types of binaries (the lighter artiards and perissads) finds its explanation in the intersection of the perissad and artiad paths at gallium.

CONCLUSIONS

1) Binary elements in the beginning of the system (to gallium) consist of pairs, in which the former are perissads and the latter artiards; after gallium, on the other hand, the former are artiards.

2) If adjacent elements, the principal isotopes of which differ in mass by one, are considered as binaries, then there are a total of 30 such binaries. If to the binaries are added those elements whose principal binaries would differ by one, if they were not artiad deviations, then another 17 pairs would be added. Thus, 94 elements consist of 47 pairs. Gallium does not form a pair; Curium will form a pair after the discovery of element No. 97.

3. The system of the principal isotopes contains two isoneutron divisions:

a. on the isoneutron No 82 ^{138}Ba ^{139}La ^{140}Ce - ^{141}Pr .

b. on the isoneutron No. 126 ^{208}Pb ^{209}Bi ^{210}Po - ^{211}At .

4. The system is divided into 4 parts by the isoneutrons No. 38, No. 82 and No. 126. The difference between $^{68}\text{Ga}^{32}$, lying on the isoneutron No. 38 and $^{139}\text{La}^{57}$, situated on the isoneutron No. 82 is 70 nucleons, that is: 26 protons and 44 neutrons. The difference between $^{209}\text{Bi}^{83}$ and $^{139}\text{La}^{57}$ is also equal to 70 nucleons: 26 protons and 44 neutrons.

5. In the number of excess neutrons of those atoms situated around argon, krypton, xenon and radon, a recurring anomaly is observed reminiscent of the Mendeleev periodicity.

6. The element weight, as well as the chemical characteristics of the elements is a special type of periodic function of the atomic number.

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TABLES

Table 1

	ΔE
Ar - K	0.848
Co - Ni	0.25
Te - I	0.69
Th - Pa	1.12
U - Np	1.07

Table 2

	ΔE	Number of iso-neutrons		ΔE	Number of iso-neutrons
B ⁵ - C ⁶	1.019	6	Se ³⁴ - Br ³⁵	0.956	44
F ⁹ - Ne ¹⁰	1.183	10	Sr ³⁸ - Yt ³⁹	1.290	50
Na ¹¹ - Mg ¹²	1.323	12	Ru ⁴⁴ - Rh ⁴⁵	1.21	58
Al ¹³ - Si ¹⁴	1.09	14	Pd ⁴⁶ - Ag ⁴⁷	1.18	60
P ¹⁵ - S ¹⁶	1.102	16	(La ⁵⁷ - Ce ⁵⁸)	1.21	82
K ¹⁹ - Ca ²⁰	0.984	20	Ce ⁵⁸ - Pr ⁵⁹	0.79	62
V ²³ - Cr ²⁴	1.06	28	(Bi ⁸³ - Po ⁸⁴)	1	126
Mn ²⁵ - Fe ²⁶	0.92	30	Po ⁸⁴ - At ⁸⁵	1	126
			Rn ⁸⁶ - Fr ⁸⁷	1	136
			Ra ⁸⁸ - Ac ⁸⁹	0.95	138
			(Am ⁹⁵ - Cm ⁹⁶)	1	146

Table 3 (1)

	ΔE		ΔE		ΔE
Li - Be	2.080	Zr - Nb	1.690	Yb ⁷⁰ - Lu ⁷¹	1.95
Be - B	1.80	Cd ⁴⁸ - In ⁴⁹	2.35	Hf ⁷² - Ta ⁷³	2.06
C - N	1.998	X ⁵⁴ - Cs ⁵⁵	1.65	W - Re	2.38
N - O	1.994	Ba ⁵⁶ - La ⁵⁷	1.56	Ir - Pt	2.13
Cu ²⁹ - Zn ³⁰	1.81	Sm ⁶² - Eu ⁶³	1.57	Pt - Au	1.97
Ge ³² - As ³³	2.31	Gd ⁶⁴ - T ⁶⁵	2.3	Pb ⁸² - Bi ⁸³	1.79
Kr ³⁶ - Rb ³⁷	1.780	Dy ⁶⁸ - Ho ⁶⁹	2.48	Np - Pu	2
Rb - Sr	2.150	Ho - Er	2.26	Pu - Am	2
Yt - Zr	2.30	Er - Tm	2.2		

There is reason to believe that the element weights of Tm, Yb, Ir and Au are not equal to 169.4; 173.04; 193.1 and 197.2, but: 168.9; 173.2; 192.2 and 197.0. Then the difference ΔE will be:

Er - Tm	1.7	Ir - Pt	3.03
Yb - Lu	1.79	Pt - Au	1.77

Table 4 1)

		ΔE			ΔE			ΔE
H - He		2.995	Cr - Mn		2.92	Pm - Sm		3.43
He - Li		2.937	Fe - Co		3.09	Tb - Dy		3.26
O - F		3.00	Ga - Ge		2.88	Ta - W		3.07
Ne - Na		2.814	Nb - Mo		3.040	Os ⁷⁶ - Ir ⁷⁷		2.9
Mg - Al		2.65	Mo ⁺² - Tc ⁺³		2.967	Au - Hg		3.41
Si - P		2.904	Tc - Ru		2.787	Tl - Pb		2.82
S - Cl		3.391	Sn ⁵⁰ - Sb ⁵¹		3.06	Fa - Ra		3.05
Sc - Ti		2.800	Pr - Nd		3.35			
Ti - V		3.05	Nd - Pm		2.73			

Table 5

⁹² Mo	14.9%			¹¹² Sn	1.1%		
⁹⁴ Mo	9.4%			¹¹⁴ Sn	0.3%		
⁹⁶ Mo	16.1%	⁹⁶ Tc	4.3 days	¹¹⁵ Sn	0.4%		
⁹⁸ Mo	16.6%	⁹⁷ Tc	95 days	¹¹⁶ Sn	15.5%		
¹⁰⁰ Mo	9.65%			¹¹⁷ Sn	9.1%		
¹⁰⁰ Mo	24.1%	⁹⁹ Tc	10 ⁶ Years	¹¹⁸ Sn	22.5%		
¹⁰⁰ Mo	9.25			¹¹⁹ Sn	9.8%		
				¹²⁰ Sn	28.5	¹²¹ Sb	56%
				¹²² Sn	5.5	¹²³ Sb	44%
				¹²⁴ Sn	6.8		

Table 6 2)

¹⁸⁴ Os	0.018%		
¹⁸⁶ Os	1.59		
¹⁸⁷ Os	1.64		
¹⁸⁸ Os	13.3		
¹⁸⁹ Os	16.1		
¹⁹⁰ Os	26.4	¹⁹¹ Ir	38.5%
¹⁹² Os	41.0	¹⁹² Ir	61.5

Table 7 3)

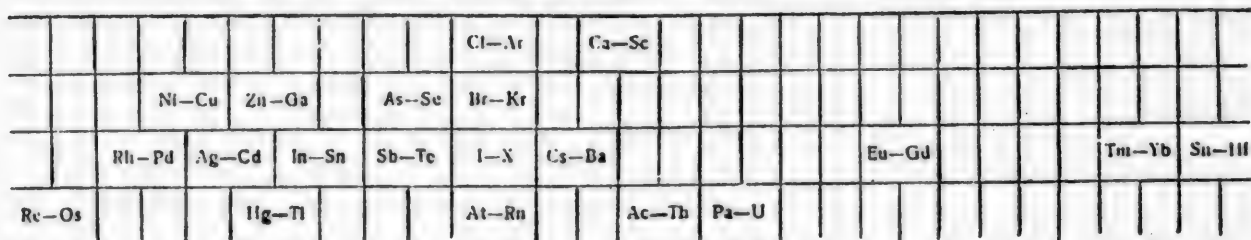
		ΔE			ΔE			ΔE
Cl - Ar		4.487	Sb - Te		5.85	Ac - Th		5.12
Ca - Sc		5.020	I - X		4.38	Pa - U		7.07
Ni - Cu		4.86	Cs - Ba		4.45			
Zn - Ga		4.34	Eu - Gd		4.9			
As - Se		4.05	Tm - Yb		3.64			
Br - Kr		3.784	La - Hf		3.81			
Rh - Pd		3.79	Re - Os		3.89			
Ag - Cd		4.53	Hg - Tl		3.78			
In - Sn		3.94	At - Ru		11			

- 1) If it is assumed that the element weights of Ru, Sm, Tb, Ir and Au are 101.1; 150.1; 158.9; 192.2 and 197.0 then ΔE becomes:

Tc - Ru	2.2	Os - Ir	2.0
Pm - Sm	3.1	Au - Hg	3.61
Tb - Dy	3.56		

- 2) In official tables, $E_{Ir} = 193.1$, but judging from the isotopic composition, this figure is exaggerated and E would be close to 192.2, i.e. $\Delta E = 2$ and not 2.9. In this case the pair Os - Ir would be relegated to the third class.
- 3) If the element weight of Tm and Yr would be 168.9 and 173.2 then ΔE for Tm - Yb would equal 4.3.

2



DIAGRAMS

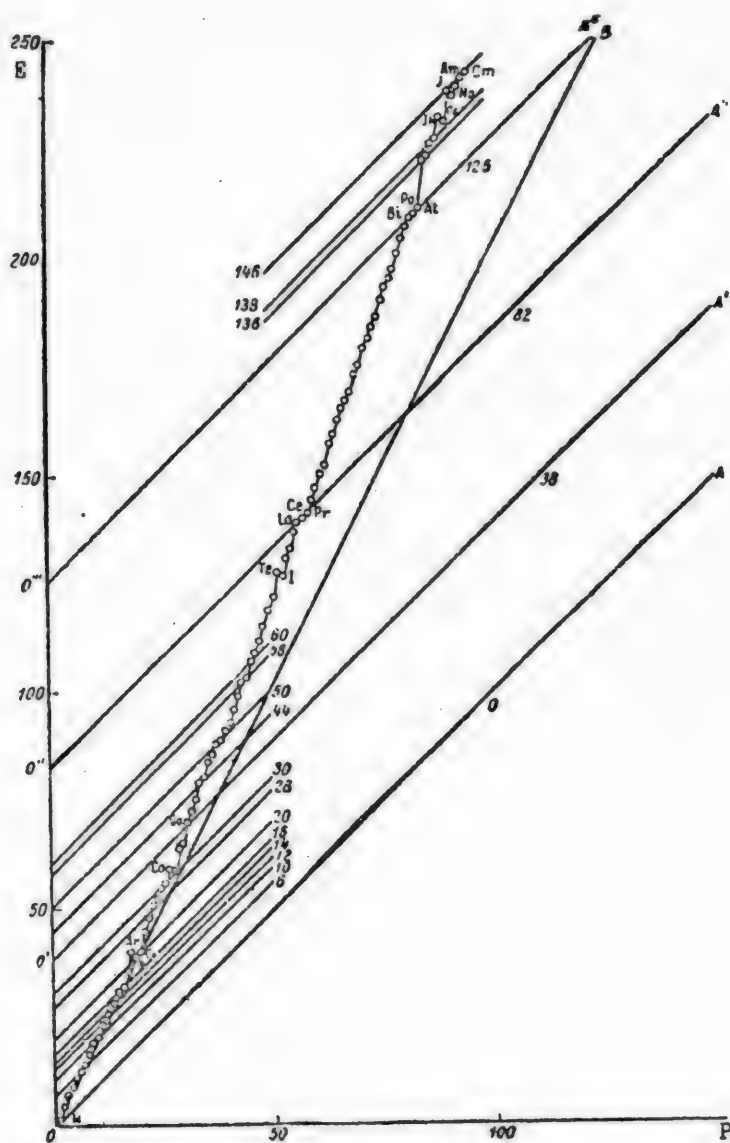


Figure 1: Element weight as a function of atomic number.



Figure 2:
Distribution
of ΔR

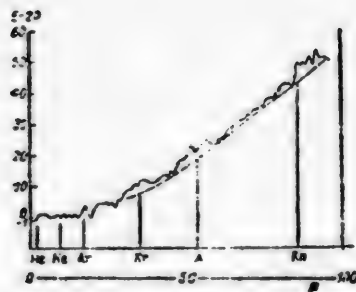
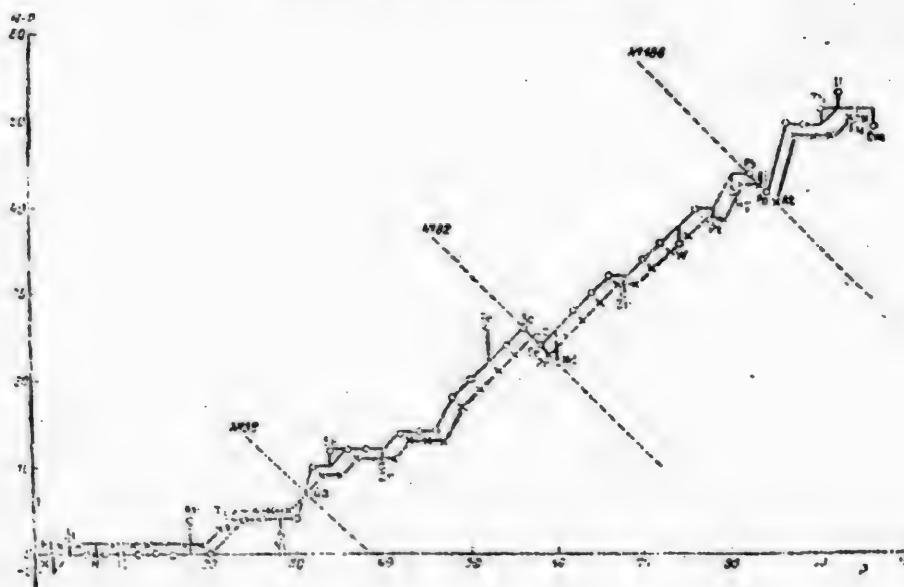


Figure 3: Quantity of
excess neutrons as a
periodic function of the
atomic number in the
Neutronium system.

Figure 4: System of the principal isotopes.



LAWS OF SOLUBILITY VARIATIONS

II. ENERGY CHARACTERISTICS OF POLYTHERMAL EUTONIC POINTS IN MULTICOMPONENT SYSTEMS

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(Leningrad)

1. Introduction

In a previous paper ¹⁾, mechanisms of polythermal eutonic points in multicomponent systems were thermodynamically examined employing the concept of nominal pressure, and the hypothesis was made that the pressure of the saturated vapor of a solution and of a pure solvent vary exponentially with the temperature.

In the present paper, which presents a logical development of this, a study is made of energy-characteristic deviations of actual equilibria for polytherms in multicomponent systems from ideal equilibria, these being determined by the law of mass action.

As examples, calculations are presented for systems with different types of solubility variations.

2. Activity Product and Solubility Product

For the equilibrium of the system:



under standard conditions

$$a = \text{constant}, \quad (2)$$

where a is the active concentration of the dissolved substance.

Let us examine the case of equilibrium (1), where the dissolved substance is the electrolyte M_rR_m which dissociates in water according to the equation:



Let us assume that under standard conditions the molar concentration of a saturated solution of an electrolyte equals L (in mols per 1000 mols of water).

We shall employ the following symbols:

for the concentrations of the ions C :

$$\left. \begin{aligned} C_m &= [M^{+m}] = rL \\ C_r &= [R^{-r}] = mL \end{aligned} \right\}, \quad (4)$$

for the active concentrations of the ions a :

$$\left. \begin{aligned} a_m &= \gamma_m C_m = \gamma_m [M+m] = \gamma_m \cdot r \cdot L \\ a_r &= \gamma_r C_r = \gamma_r [R-r] = \gamma_r \cdot m \cdot L \end{aligned} \right\} \quad (5)$$

where γ_m and γ_r are the activity coefficients:

In conformance with condition (2), we have:

$$K_a = a_m^r \cdot a_r^m = \gamma_m^r \cdot \gamma_r^m \cdot r^r \cdot m^m \cdot L^{m+r} = \text{constant} \quad (6)$$

where K_a is the activity product 2).

If the activity coefficient approaches one, then it follows from equation (5) that the active concentration of the ions become equal to the concentration of the ions, i.e.

$$\left. \begin{aligned} \lim a_m &\rightarrow C_m \\ \gamma_m &\rightarrow 1 \\ \lim a_r &\rightarrow C_r \\ \gamma_r &\rightarrow 1 \end{aligned} \right\} \quad (7)$$

The activity product under the conditions of (7) is called the solubility product:

$$\left. \begin{aligned} \lim K_a &= K_0 \\ \gamma &\rightarrow 1 \end{aligned} \right\} \quad (8)$$

the magnitude of which as calculated from equation (6), indicates that the activity coefficients are equal to one:

$$K_0 = C_m^r \cdot C_r^m = m^m \cdot r^r \cdot L^{m+r}. \quad (9)$$

3. Characteristic of an Actual Equilibrium

Introducing the magnitude φ , we define it as

$$\varphi = \frac{K_0}{K_a}; \quad (10)$$

it appears in saturated solution as a measure of the deviation for each individual component from the actual equilibrium in a multicomponent system and is determined from the activity product for an ideal equilibrium and from the solubility product in two component systems: the electrolyte in this case being water.

From equations (6) and (9) it follows:

$$\varphi = \frac{1}{\gamma_m^r \cdot \gamma_r^m} \quad (11)$$

i.e. the greater the activity product differs from the solubility product, the greater is the difference of the activity coefficient from one, and the greater the magnitude of m and r .

The magnitude of φ can assume the following denotations:

- 1, where $\gamma_m^r \cdot \gamma_r^m < 1$, $\varphi > 1$: this corresponds to the case when the actual equilibrium is less than the theoretical;
- 2, where $\gamma_m^r \cdot \gamma_r^m = 1$, $\varphi = 1$; this corresponds to the ideal behavior of a dissolved substance;
- 3, where $\gamma_m^r \cdot \gamma_r^m > 1$, $\varphi < 1$; this corresponds to the case when the actual equi-

librium is greater than the theoretical:

Therefore, in general it can be written:

$$\varphi \gtrsim 1. \quad (12)$$

4. Energy Characteristic of an Actual Equilibrium

For process (1), the equilibrium constant of which is characterized by a constant activity product (6), the following equation is valid.

$$\Delta F_a = -RT \ln K_a \quad (13)$$

where ΔF_a is the loss in free energy of the system in the examined process and T is the absolute temperature.

For the situation determined by conditions (7), equation (13) can be rewritten in the following manner:

$$\Delta F_c = -RT \ln K_c. \quad (14)$$

Let us examine the difference in the variations of the free energies ΔF_c and ΔF_a :

$$\Delta F = \Delta F_c - \Delta F_a. \quad (15)$$

This difference is the energy characteristic deviation of the actual equilibrium in the system from the ideal equilibrium.

Substituting in equation (15) the symbols for free energies from equations (13) and (14) and taking equation (10) into consideration, we obtain:

$$\Delta F = -RT \ln \varphi. \quad (16)$$

From equation (16) it follows that the magnitude of φ can be considered as a reduced equilibrium constant in a saturated solution.

Corresponding to equation (12) we can then state:

$$\Delta F \lesssim 0. \quad (17)$$

5. Basic Symbols

Let us take a three-component water-salt system, for example, one with the same monovalent anion R:



Let us assume that under these conditions the formation of chemical compounds between the components of the solution does not occur.

In the given case the solubility isotherm will consist of two branches, corresponding to the solid phases MR_m and MR_n , crossing at the eutonic point.

The basic symbols for solubilities (in mols per 1000 mols H_2O) and for other magnitudes are presented in Table 1.

Table 1:
Basic Symbols

	In general	Components	
		"1"	"2"
Individual solubility	L	L_1	L_2
Mutual solubility for polytherms.	l	l_1	l_2
Reduced equilibrium constant for polytherms	φ	φ_1	φ_2
Change in free energy for polytherms	ΔF	ΔF_1	ΔF_2

6. Polythermal Variations of the Reduced Equilibrium Constants and of the Free Energies

Let us examine the polythermal variations of the reduced equilibrium constants and of the free energies for the eutonic points in three component systems.

Using the symbols given in Table 1, the following formulas are obtained: for the reduced equilibrium constants:

$$\left. \begin{aligned} \varphi_1 &= \frac{m^m L_1^{m+1}}{l_1(m l_1 + n l_2)^m} \\ \varphi_2 &= \frac{n^n L_2^{n+1}}{l_2(m l_1 + n l_2)^n} \end{aligned} \right\} ; \quad (19)$$

for the variations of free energy:

$$\left. \begin{aligned} \Delta F_1 &= -4.5787 \, T \lg \varphi_1 \\ \Delta F_2 &= -4.5787 \, T \lg \varphi_2 \end{aligned} \right\} . \quad (20)$$

As was shown in a previous work ¹⁾, the individual and mutual solubilities change exponentially with the temperature.

$$L = \exp \left(\frac{A}{T} + B \right) \quad (21)$$

$$l = \exp \left(\frac{a}{T} + b \right) \quad (22)$$

Removing L and l from equation (19) by the use of formulas (21) and (22), we may, by applying the theory of series, express the reduced constant (19), with a sufficient degree of accuracy as:

$$\varphi = \exp \left(\frac{A_\varphi}{T} + B_\varphi \right) \quad (23)$$

or logarithmically as:

$$\ln \varphi = \frac{A_\varphi}{T} + B_\varphi \quad (24)$$

where A_φ and B_φ are constants.

From equation (24) it follows that on the axes $\lg \varphi$, $\frac{1}{T}$ the logarithms of the reduced constants should be expressed on the graph as a straight line.

Substituting φ from equation (24) to equation (20), we obtain:

$$\Delta F = A_F + B_F \cdot T, \quad (25)$$

where A_F and B_F are constants.

From equation (25) it is seen that the change in free energy with temperature follows a straight line.

7. Examples

As examples, confirming the accuracy of the conclusions obtained on the relationship of the reduced constant of an equilibrium and the change of free energy with temperature, we will present appropriate data on ternary polythermal systems with various characteristics of solubility change

1) $\text{NaCl} - \text{KCl} - \text{H}_2\text{O}$

The given ternary system is characterized by the fact that the combined solubility

at the eutonic point is less than the individual solubilities.

Calculations, derived from the experimental data of Kurnakova and Osokorevoi³⁾ and Korneka and Krombakha⁴⁾ are shown in Table 2. The calculated results are shown by the illustrations: relationship of $\lg \Phi$ with $\frac{1}{T}$ given in Figure 1 and the relationship of ΔF with T in Figure 2.

The data of Kurnakova and Osokorevoi are indicated by crosses, that of Korneka and Krombakha by circles.

From the two sets of experimental data on solubility (Table 2) it is evident that they differ somewhat from each other, which in turn causes significant deviations in $\lg \Phi$ and ΔF .

For sodium chloride the change in $\lg \Phi_1$ and ΔF_1 follow equations (24) and (25).

For potassium chloride the deviation is greater, as a result of which the change in $\lg \Phi_2$ and ΔF_2 is not as clear.



The given ternary system is characterized by the fact that the combined solubility at the eutonic point is greater than the individual solubility.

The calculations, based upon the experimental data of Reinders⁵⁾ are shown in Table 3. The calculated results shown in Figure 3 indicate that formulas (24) and (25) are also accurate in this case.

8 Conclusions

- 1) A study was made of deviations of actual equilibria from ideal equilibria for components at the eutonic point of systems obeying the law of mass action.
- 2) The concept was presented of a reduced equilibrium constant, characterizing the actual status of a component in a system.
- 3) It was shown that the logarithm of the reduced equilibrium constant varies with the change in free energy of a component in a system.
- 4) It was brought out that the reduced equilibrium constant varies exponentially with the reciprocal of the temperature.
- 5) It was shown that a straight line relationship exists between the change in free energy for a component in a system and the temperature.
- 6) Examples are given, demonstrating the accuracy of the conclusions obtained.

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Table 2
Polythermal System NaCl - HCl - H₂O

Data in gram-mol per 1000 gram-mol H₂O

T, °C	x _{HCl}	$\frac{1}{T}$	NaCl		HCl		reduced equilibrium constants		T ₀	T ₀₀	change in free energy	
			I ₁	I ₂	I ₃	I ₄	z ₁	z ₂			-ΔF ₁	ΔF ₂
Data of Kurnukova and Osoverov 3)												
0.28	0.001334	116.14	91.69	76.72	41.32	1.018	1.000	0.00775	0.17319	1004	224.4	
20.29	0.001113	110.38	91.99	83.48	38.16	1.019	1.001	0.00817	0.1737	9926	197.7	
40.29	0.001376	110.98	91.94	87.20	39.32	1.021	1.073	0.00933	0.16839	1232	220.0	
60.40	0.001709	111.75	91.20	90.10	42.40	1.020	1.433	0.00890	0.15625	11294	216.8	
80.11	0.002105	112.60	90.82	97.74	47.74	1.008	1.411	0.00930	0.15957	4259	228.7	
100.12	0.002406	113.58	88.95	103.84	54.00	1.014	1.397	0.00960	0.14534	8433	214.7	
120.33	0.003003	114.10	88.62	110.14	59.88	0.9834	1.372	0.00967	0.13735	-7120	209.4	
140.11	0.003915	116.12	88.12	116.14	66.82	0.9874	1.309	0.00942	0.11691	-8512	183.7	
160.35	0.005233	116.80	85.38	122.20	72.48	1.012	1.305	0.00918	0.11561	8372	186.9	
180.36	0.00775	119.70	87.05	129.00	78.52	1.030	1.296	0.00920	0.11261	2134	187.2	
100.37	0.00581	121.58	84.54	136.08	85.32	1.028	1.273	0.01190	0.10183	2848	179.0	

Data of Kornek and Krasbavsk 4)

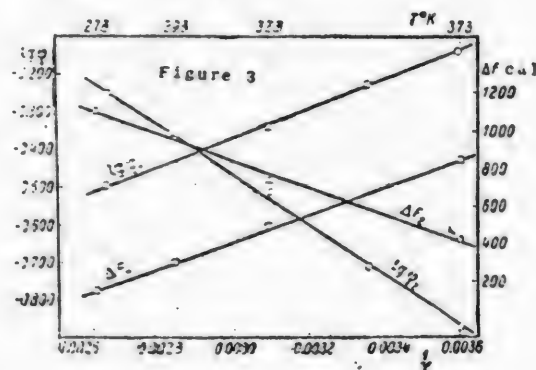
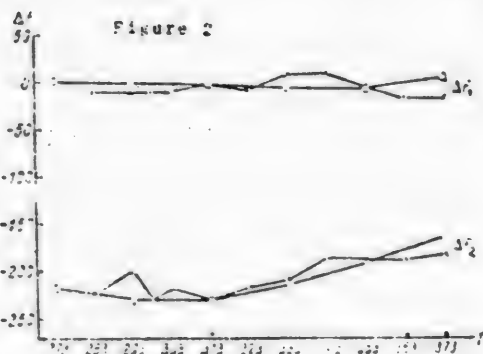
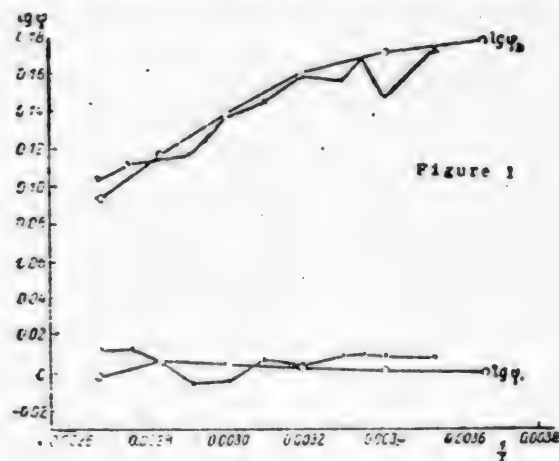
0.273	0.001995	109.7	98.01	67.90	24.88	0.9992	1.508	0.00933	0.17411	-64123	217.9	
20.26	0.003113	110.3	93.69	82.88	35.73	1.003	1.481	0.00940	0.17155	1878	200.2	
40.31	0.003197	111.9	90.30	97.14	47.95	1.007	1.448	0.00916	0.16058	4529	230.1	
60.33	0.003003	114.1	87.51	109.7	59.45	1.012	1.377	0.00916	0.13901	7868	212.0	
80.35	0.003283	116.8	87.57	122.3	72.49	1.015	1.310	0.00929	0.11736	1017	189.6	
100.37	0.00581	119.2	80.76	134.1	85.22	0.9977	1.212	0.00910	0.09387	-1703	160.3	

Table 3

Polythermal System NaNO₃ - KNO₃ - H₂O

Data in gram-mols per 1000 gram-mols H₂O

T, °C	x _{NaNO₃}	1/T	NaNO ₃		KNO ₃		reduced equilibrium constants		-15%	-10%	change of free energy	
			I ₁	I ₂	I ₃	I ₄	z ₁	z ₂			ΔF ₁	ΔF ₂
0.278	0.000397	161.71	174.00	20.99	32.25	0.7287	0.1352	0.13745	0.86902	1550	1106	
20.298	0.00336	194.09	213.85	69.23	82.24	0.5986	0.1968	0.22266	0.70597	204.1	963.3	
50.323	0.00494	241.82	285.91	151.64	160.73	0.4579	0.3203	0.35423	0.49444	501.7	731.2	
100.373	0.00681	373.92	195.09	438.35	388.46	0.3181	0.5598	0.49744	0.25197	84.2	430.3	



EQUILIBRIUM OF THE SYSTEM $\text{NaF} - \text{AlF}_3 - \text{H}_2\text{O}$

V. S. Yatlov and E. N. Pinaevskaya

Up to the present time it was believed that two sodium fluoroaluminates existed in nature: cryolite, with the formula Na_3AlF_6 , and chiolite, to which the formula $5\text{NaF} \cdot 3\text{AlF}_3$ has been ascribed.

From a study of the phase diagram for the system $\text{AlF}_3 - \text{NaF}$ Fedotiev and Ilinski^[1] established the existence of these fluoroaluminates. They also observed that cryolite forms mixed crystals with aluminum fluoride. Concerning the formation of mixed crystals their results agree with the observation of Lorentz et al^[2]. An investigation of the equilibrium in this system carried out by Pushin and Baskov^[3] gave results agreeing in general with those of Fedotiev and Ilinski, but they ascribed the formula $3\text{NaF} \cdot 2\text{AlF}_3$ to cryolite. Up to now a systematic investigation in an aqueous medium has not been carried out. Very few observations on the production of individual fluoroaluminates have been encountered in the literature.

Berzilius^[4], C. K. Deville^[5], and Kugler^[6] have reported on the production of sodium hexafluoroaluminate from aqueous solutions. Beau^[7] indicated the possibility of obtaining cryolite as the hydrate of the hexafluoroaluminate, $\text{Na}_3\text{AlF}_6 \cdot 3.5\text{H}_2\text{O}$, by mixing equivalent quantities of the fluoride solutions. However, upon further tests^[8] Beau's findings were not confirmed. The cryolite obtained under such conditions did not contain water of crystallization, and the molecular ratio of $\text{Na} : \text{Al}$ in the precipitate obtained was 2.7 - 2.8. The same composition is characteristic of a precipitate prepared under other conditions, in particular the precipitate separating at 75°C upon the complete neutralization of fluoroaluminic acid with sodium hydroxide.

Upon partial neutralization with sodium hydroxide (0.1 equivalents were taken), a precipitate separates at the same temperature with a ratio of $\text{Na} : \text{Al}$ close to one.^[8]

Tananaiev and Talipov^[9] confirmed the fact that upon addition of a solution of AlCl_3 to a solution of sodium fluoride, in the ratio $\text{Na} : \text{Al} = 8$ (but not added in the opposite order), they obtained a precipitate exactly similar to that of the hexafluoroaluminate, although they did not analyze the precipitate obtained. In a later work, appearing in print after the completion of our work, one of the former authors, Tananaiev^[10, 11], based upon systematic investigations concluded that two fluoroaluminates existed. The hexafluoroaluminate, an incongruently soluble compound, exists in equilibrium with solutions containing over 1.4% NaF . Where the concentration of sodium fluoride is lower the composition of this incongruently soluble compound corresponds to the formula $11\text{NaF} \cdot 4\text{AlF}_3$.

Assuming the existence of the hexafluoroaluminate as a stable compound in aqueous solution, it indicates that the molar ratio $\text{NaF} : \text{AlF}_3$ in natural cryolite is 2.72 - 2.75.

The application of electrolytic methods did not throw much light on the question of the equilibrium in the given system.

Tosterud^[12], measuring the electrical conductivity of fluoroaluminate solutions found that the maximum resistance of the solution corresponded to a molar ratio of $\text{Na} : \text{Al} = 1.5$.

Riss and Zhukov [13], using the same method, conducted a more systematic investigation of the equilibrium in the given system, but as a result of an incorrect selection of the Na:Al ratio it is impossible to draw any kind of conclusion from their results.

The data in the literature show such variation in the composition of the double fluorides of the two metals, and neither does it throw light upon the conditions for the equilibrium of the system $\text{NaF} - \text{AlF}_3 - \text{H}_2\text{O}$. However, investigation of the equilibrium in this saline system is of great practical importance as a basis for the manufacture of cryolite.

Starting Materials and Method

As starting materials for the investigation of the equilibrium in the given system, sodium fluoride and the trihydrate of aluminum fluoride were used as well as the fluoroaluminate, prepared by the neutralization of fluoroaluminic acid with sodium hydroxide. Sodium fluoride was prepared by the double decomposition reaction between solutions of ammonium fluoride and sodium carbonate, drying the precipitate at 100°C and then heating it at around 700°C . The ammonium fluoride was prepared from c.p. hydrofluoric acid by saturating it with gaseous ammonia and doubly recrystallized Na_2CO_3 . The aluminum fluoride was obtained from metallic aluminum and c.p. hydrofluoric acid.

Since the given system is characterized by low concentrations, it was found necessary to prepare large volumes of the equilibrium solutions. Since the amount of the solid phase was quite small in relation to the large volume of solution, a change in its composition did not cause a significant change in the composition of the starting solutions. To ensure high accuracy in analytical determinations it was necessary to take large quantities of the solutions, in several cases amounting to 200 grams.

The composition of the solid phase was established by analysis of the precipitate separating out from the equilibrium solution and washing it with water, alcohol and ether. In several cases the double "residue" method of Schreinemakers was used for verification. Here the radial structure of crystallization for each solution was used for analyzing the double "residues". This method was used since the plotting of various points of the solution and the "residue" on a graph with equal divisions was not a practicable possibility.

The solid phase was also studied microscopically, the index of refraction being determined by the immersion method. The electrical conductivity method was also used to investigate the equilibrium in the given system.

The measurement of electrical conductivity by means of the Wheatstone bridge was carried out according to the procedure developed by Semienchenko et al. [14].

The structure of the cell was taken from that of Riss and Zhukov [13].

For measurements at a temperature of 25°C , the cell as well as the vessel for preparing the equilibrium solutions (which were carried out in a thermostat for 6-8 days) were covered with a layer of carefully purified paraffin. At a temperature of 75°C the work was conducted in glass, the test being kept for a shorter time in the thermostat. For measurement of electrical conductivity the cell was placed in the thermostat.

Experimental Results and Discussion

In Table 1 are shown results of analyses of saturated solutions, and the solid phases in equilibrium with these solutions, obtained at the temperature of 75°C .

A study of the given system, as noted above, presented great difficulties. The concentration of each component was changed hundreds of times, lowering them to very small concentrations. In solutions containing NaF in amounts greater than 0.4% the usual gravimetric

The apparatus was set up with the assistance of A. A. Chierbakov, a scientific coworker of the Institute.

methods were not successful in revealing the presence of aluminum, notwithstanding the weight, which reached 200 grams. On the other hand, in solutions with a high concentration of AlF_3 , the detection of very small changes in the concentration of NaF could be carried out only at the expense of accuracy in the analyses. As a result the change in composition of the solution in this region is not definite. These difficulties make it practically impossible to represent the results graphically.

The investigation of solid phases by the application of the double residue method of Schreinemakers was hindered by the fact that the various points of different solutions, even with such large segments as those of the chiolite crystallizations, were shown to lie on a straight line. This is explained by the fact that the solubility curves of the solutions merged into one point when a practical scale of units was used.

The radial crystallizations for the last two solutions shown in Table 2 are also practically identical, in spite of the fact that the NaF concentration in one is double that of the other. Therefore this method could not be used to determine the composition of the solid phases formed by chiolite and aluminum fluoride. It is obvious, then, that the solubility curve in this region should be characterized by a very small spread.

Determination of the index of refraction for the solid phases also met with difficulty, caused by the small differences in their magnitudes and also by the small size of the crystals. Although the index of refraction does not present a completely clear picture it does, to some degree, facilitate the interpretation of the analytical results.

First it must be shown that the determination of the crystal refractions established the uniformity of the crystals in those solid phases the composition of which is given in Table 1.

According to the index of refraction, four groups of solid phases can be differentiated.

In the first group are included those solid phases (experiments 1-2, Table 1) which by composition and index of refraction correspond to the trihydrate of aluminum fluoride.

The incompletely described crystals of the second group (experiments 3-5, Table 1,) have varying compositions and are found in equilibrium with solutions of varying composition. Their indices of refraction are also not constant. In form, the crystals of the second group are reminiscent of the trihydrate. Here very small aggregates were observed amid separate small crystals. The variations in this small section qualitatively comply with the formation of solid solutions.

The third group of solid phases (experiments 7-11, Table 1) consists of crystals of constant composition and practically identical indices of refraction and at the same time are found in equilibrium with solutions of varying compositions. Therefore, definite compounds exist in this section.

The fourth group of solid phases (experiments 12-21, Table 1) consists of precipitates of varying composition, found in equilibrium with solutions of different concentrations. Some of the indices of refraction for crystals in this group could not be obtained.

Thus, it can be definitely stated that only one compound exists in this system besides the trihydrate of aluminum fluoride. The composition of this compound corresponds to that of the natural mineral chiolite $5\text{NaF} \cdot 3\text{AlF}_3$, and also to the composition of the chiolite $3\text{NaF} \cdot 2\text{AlF}_3$, discovered in the study of the anhydrous system $\text{AlF}_3 - \text{NaF}$. According to our analyses the composition of this compound averages $1.56\text{NaF} \cdot \text{AlF}_3$, closer to the formula given by Pushin and Baskov [3] $3\text{NaF} \cdot \text{AlF}_3$, than to the formula of natural chiolite as determined by Fedotiev and Ilinski [1].

The fluoroaluminate in question crystallizes from solutions containing AlF_3 from

Table 1

Exp. No.	Initial components		Equilibrium solution contains		Solid phase contains			Loss upon heating at 600°C (%)	$\frac{[Na]}{[Al]}$ in the solid phase	Index of refraction
	Solution contains (in %)	Salt	AlF ₃ (%)	NaF (%)	P (%)	Al (%)	Na (%)			
1	-0.015	AlF ₃ ·3H ₂ O	0.89	not determined	42.91	19.85	—	39.52	—	1.410
2	-0.03	The same	0.93	0.018	41.17	19.99	—	39.28	—	1.409
3	-0.08	"	0.93	0.032	49.81	20.84	11.94	17.56	0.63	1.336
4	-0.11	"	0.96	0.032	52.78	20.36	15.24	10.19	0.68	1.365
5	-0.14	"	0.69	0.033	—	20.00	15.25	11.58	0.90	1.369
6	-0.75	Chiolite	0.75	0.038	56.03	19.67	22.40	4.87	1.34	1.360
7	-0.89	Cryolite	0.72	0.049	55.63	18.33	24.20	2.33	1.55	1.351
8	-0.50	Chiolite	0.50	0.046	55.05	18.30	24.65	1.73	1.51	1.351
9	-0.25	the same	0.25	0.035	55.07	18.27	24.31	2.07	1.56	1.355
10	-0.10	"	0.143	0.033	55.59	18.10	23.75	2.17	1.54	1.351
11	-0.05	"	0.093	0.048	55.59	18.76	24.19	not determined	1.55	1.355
12	Water	AlF ₃ ·3H ₂ O and NaF	0.014	0.051	54.71	16.72	27.27	1.2	1.92	—
13	NaF -0.1	Chiolite	0.016	0.073	53.60	15.82	28.36	3.13	2.14	1.343
14	Water	AlF ₃ ·3H ₂ O and NaF	0.0105	0.069	53.44	14.55	30.32	2.04	2.44	—
15	-0.2	Chiolite	0.006	0.082	54.30	13.85	32.49	3.40	2.81	1.343
16	-0.5	The same	not found	0.40	53.10	14.41	32.62	not determined	2.66	1.310
17	-1.0	"	The same	0.88	53.40	14.18	32.00	2.70	2.66	—
18	-2.0	"	"	1.83	53.30	13.63	32.05	2.04	2.70	—
19	-3.0	"	"	2.62	52.82	13.84	31.89	1.68	2.69	—
20	-4.0	"	"	3.86	53.68	13.65	32.78	2.14	2.75	—
21	-4.0	Cryolite	"	4.05	53.02	13.68	32.38	1.96	2.78	—

Table 2

Exp. No.	Solution contains				Precipitate contains				$\frac{[Na]}{[Al]}$ in the solid phase
	Initially		at equilibrium		1		2		
	AlF ₃ (%)	NaF (%)	AlF ₃ (%)	NaF (%)	AlF ₃ (%)	NaF (%)	AlF ₃ (%)	NaF (%)	
1	0.85	—	0.86	—	21.24	16.10	33.54	25.80	1.56
2	0.70	—	0.73	—	21.10	18.49	33.13	26.03	1.56
3	0.55	—	0.60	—	18.04	13.80	32.78	26.80	1.56
4	0.40	—	0.46	—	20.46	15.70	33.50	25.35	1.56
5	0.25	—	0.29	0.032	4.84	3.54	26.55	20.60	1.56
6	—	0.5	Not found	0.35	24.50	34.55	31.10	43.10	2.66
7	—	1.9	The same	0.82	21.74	30.07	30.39	40.39	2.67

Table 4

Exp. No.	Conditions for obtaining the fluoroaluminate	Fluoroaluminate content			Index of refraction at 600°C (%)	$\frac{[Na]}{[Al]}$ in the fluoroaluminate
		P (%)	Al (%)	Na (%)		
1	According to Tumanov [6]	54.77	13.35	30.60	3.54	2.69
2	From fluoroaluminic acid	52.95	13.70	31.82	1.45	2.73
3	By isothermal evaporation	52.68	13.35	31.20	not determined	2.74

Table 3 (Temperature 75°C)

Exp. No.	Concentration of solution in % AlF ₃	Fluoroaluminate content			Loss upon heating at 600°C (%)	$\frac{[Na]}{[Al]}$ in the fluoroaluminate
		P (%)	Al (%)	Na (%)		
1	10	50.01	19.34	15.87	15.16	0.97
2	20	51.90	18.97	16.27	12.60	1.01
3	7.5	52.70	19.38	15.66	10.02	0.95
4	5.0	51.39	19.35	16.54	11.4	1.03

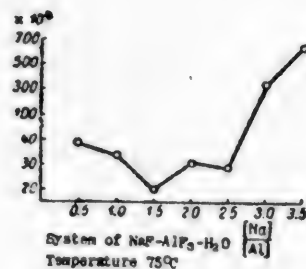


Table 5 (Temperature 75°C)

Exp. No.	$\frac{[Na]}{[Al]}$ in initial components	Resistance of the solution (Ω)	Specific elec. conduct. of sol.	Equilibrium solution contains		Solid phase contains			Loss on heating at 600°C (%)	$\frac{[Na]}{[Al]}$ in the solid phase
				AlF ₃ (%)	NaF (%)	P (%)	Al (%)	Na (%)		
1	0.5	84.9	3.8	0.89	0.029	52.45	19.97	16.34	8.8	0.96
2	1.0	93.7	3.5	0.54	0.039	54.37	19.34	20.78	5.12	1.25
3	1.5	155.4	2.1	0.14	0.044	55.92	18.44	24.29	1.08	1.55
4	2.0	103.2	3.1	0.014	0.051	54.71	16.72	27.27	1.20	1.92
5	2.5	109.9	2.9	0.0105	0.060	53.94	14.55	30.32	2.04	2.44
6	3.0	9.2	35.1	0.0068	0.65	52.45	14.84	29.85	3.99	2.41
7	3.5	5.1	63.1	0.0028	1.38	52.17	14.53	28.55	4.85	2.31

0.76 to 0.09%, with a practically constant concentration of NaF.

Upon further decreasing the concentration of aluminum fluoride the NaF content in the solution begins to increase, the concentration of the solid phase components gradually changing towards an increase in the NaF:AlF₃ molecular ratio. But even when the equilibrium solution is saturated with NaF, the precipitate obtained possesses the molecular ratio NaF:AlF₃ = 2.7 - 2.8. For this reason the crystallization of the hexafluoroaluminate from aqueous solution was not attained. The variable composition of solutions in this region and the changing composition of the precipitates associated with these solutions in the equilibria (see experiments 12-21, Table 1), indicate the presence in the solid phase of solid solutions of chiolite in aluminum fluoride.

Also, when the concentrations of aluminum fluoride is higher than solutions of chiolite, the concentration of precipitates with variable compositions is explained by the formation of solid solutions of chiolite in aluminum fluoride.

In conformance with the above concerning the quantity and properties of the precipitates formed as well as the phase changes occurring, an equilibrium diagram for the given system may be formulated. It may be noted that the equilibrium is composed of five segments. The first segment is that for the crystallization of aluminum fluoride. The second, concerning which we can only discuss hypothetically, is that of the crystallization of solid solutions of chiolite in aluminum fluoride. The third segment, the largest, is that of a saturated solution of chiolite, and with a noticeable sharp break this segment proceeds to the next segment of solid solutions of chiolite in sodium fluoride. The last segment follows, that of the crystallization of sodium fluoride, which we did not investigate.

The results of Table 3 confirm the observations of Yatlov [8] on the possibility of separating from concentrated solutions of fluoroaluminates the tetrafluoroaluminate corresponding to the formula NaF · AlF₃, which does not crystallize from solutions as a stable solid phase.

All of the precipitates with the exception of the third were obtained by saturating an almost neutral solution of aluminum fluoride with sodium fluoride. The sodium fluoride was added as a solution in an amount not exceeding 0.1 parts over that amount required for the complete combination of AlF₃ as the tetrafluoroaluminate. The third precipitate was obtained by saturating a solution of fluoroaluminic acid with sodium hydroxide added in a quantity of 0.1 parts less than the amount required for complete neutralization.

Thus, independent of the concentration of the solution (within the limits 5 - 20% AlF₃, and its initial acidity a precipitate of the tetrafluoroaluminate could be formed at 75°C, the composition of which is rather similar to the composition of the monoaqueous salt. The fluoroaluminate corresponding to the formula 3NaF · AlF₃ not only was not found in a stable form, but our observations refuted the possibility of obtaining it even in the form of a metastable phase.

Under the conditions described by Tananaiev [9] for obtaining it as well as precipitation from fluoroaluminic acid with a Na:Al ratio in the initial components of 3.5, we could only obtain a fluoroaluminate with a ratio of Na:Al = 2.7 - 2.8. The compositions of the fluoroaluminates are shown in Table 4.

It should be noted that a precipitate of the composition shown in Table 4, experiment 3, having a well defined octahedral form and up to several μ in size was obtained using an isothermal evaporation at 75°C of a solution with an initial concentration of 0.014% AlF₃ and a molecular ratio Na/Al = 4.1.

In Table 5 and on the diagram are given the results of electrical conductivity

measurements of saturated solutions obtained by dissolving solid $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ and NaF - at a temperature of 75°C . In the table are also found analytical data characterizing the composition of these solutions and the solid phases found in equilibrium with them.

The formation of chiolite, as is evident from Table 5 and the diagram (experiment 3) is distinguished by a drop in the specific electrical conductivity of the solution saturated with the given solid phase. The specific electrical conductance is here lowest of all, this being evidently connected with the lowest solubility of the solid phase.

The type of specific electrical conductivity change observed at 75°C is repeated at 25°C . In this case the solution saturated with chiolite has the smallest specific electrical conductance. The formation of solid solutions of chiolite with sodium fluoride causes a gradual increase in the electrical conductivity of the solutions until a solution is reached in which the solid phase appears as a solid solution with the maximum $(\text{Na}):(\text{Al})$ ratio. Then a sharp increase in the electrical conductivity takes place.

It may be surmised that the sharp rise in specific electrical conductance observed at either temperature, beginning with a molecular ratio of 2.4, may be explained by the solubility limit of chiolite in the solid sodium fluoride. It must be noted that the limit of solubility as determined by the electrical conductivity method is lower than the limit obtained by the determination of the precipitate composition according to the method of Schreinemakers.

CONCLUSIONS

1. A partial investigation of the isothermal equilibrium of the system $\text{NaF} - \text{AlF}_3 - \text{H}_2\text{O}$, using the thermostatic method as well as the electrical conductivity method established the fact that besides the trihydrate of aluminum fluoride there exists only one compound, corresponding in composition to natural chiolite.
2. This compound forms an uninterrupted series of solid solutions with aluminum fluoride (supposedly) and sodium fluoride, in which the molecular ratio $\text{Na}:\text{Al} = 2.7 - 2.8$ is governed by the limit of solubility of solid chiolite in sodium fluoride.
3. The sodium hexafluoroaluminate was not separated even in the form of a metastable compound.
4. The existence of sodium tetrafluoroaluminate as a stable phase was not shown, but it was established that it could be separated as a monoaqueous salt from concentrated solutions of aluminum fluoride.
5. The double fluoride of sodium and aluminum is incongruently soluble in water.
6. Based upon the results of the investigation, the solubility curve consists of 5 (4) segments: the segment for the crystallization of aluminum fluoride which shifts, conditionally, into the segment of solid solutions of chiolite in aluminum fluoride. The largest segment of all is next - that of the crystallization of chiolite. The fourth segment is that of a solid solution of chiolite in sodium fluoride, and finally the fifth, which we did not investigate, and is the segment for the crystallization of sodium fluoride.

LITERATURE CITED

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THE MUTUALLY IRREVERSIBLE SYSTEM OF POTASSIUM AND CALCIUM

CHROMATES AND NITRATES

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A study of the phase diagram for potassium and calcium chromates and nitrates was undertaken because of the need of the petroleum industry for a good saliferous heating medium, having a low melting point (160°C) and thermally stable up to $450^{\circ} - 500^{\circ}\text{C}$. All the components of the given system are strong iron corrosion inhibitors; therefore this heating medium, it seems to us, is of definite interest for industry and in particular for the catalytic cracking industry.

The excellent work of A. P. Rostkovski [1] served as a basis for the study of the given system. He showed that the eutectic temperature of the binary system $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$ is found at 145°C . Such a low melting temperature of the nitrate mixtures led us to believe that the introduction of chromates into the melt would lower this temperature still more, thus leading to the possibility that the low temperature limit of the chromate heating medium would be acceptable to industry.

However, the data of A. P. Rostkovski for the binary system $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$ differed markedly from the results of Menzies and Dutt [2] who showed that this system had a simple eutectic at 210°C . For our purpose a eutectic temperature of 210°C was useless, being too high. Therefore we decided to test the data of both authors. Visual observations of several points of the binary system $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$ indicated an almost complete similarity of our data with the data of A. P. Rostkovski. For a more precise determination of the eutectic temperature we studied the heating curve for 51 mol% $\text{Ca}(\text{NO}_3)_2 + 49 \text{ mol } \% (\text{KNO}_3)_2$ which indicated a eutectic pause at 142°C . The heating curve was studied by the use of Engineer Simonov's automatically recording pyrometer.

Thus, the lower temperature limit of the binary system, being equal to 142°C , was fully applicable as a basis for the study of the composition of the chromate - nitrate heating medium. The question of the top temperature limit is of interest only in relationship to the thermal instability of calcium nitrate, which decomposes at a somewhat higher temperature than that of its melting point. But the melting point of calcium nitrate, in any case, is greater than 500°C , being equal to 560°C according to the data of Afonski and Kroschkin [4] and A. P. Palkin [5]. According to our observations the melting point of $\text{Ca}(\text{NO}_3)_2 = 530^{\circ}\text{C}$.

Concerning potassium nitrate, A. G. Bergman showed in his investigations that it was thermally stable up to almost 600°C , and that potassium and calcium chromates were thermally stable even at a much higher temperature. Since for the purposes of catalytic cracking a temperature of 450°C is required, it is evident that the heating medium of potassium and calcium chromates and nitrates should be applicable to industry not only because of its low melting point but also because of its satisfactory thermal stability.

Because of the decomposition of the nitrates the diagram of this mutual system could be investigated only up to 530°C. Also, since the reaction sharply proceeds to the side of the stable pair $(\text{KNO}_3)_2 - \text{CaCrO}_4$, the portion of the diagram we studied is not large and tends toward the quadrant $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$.

BINARY SYSTEMS

1. The Binary System $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$

The system of potassium and calcium nitrates was first studied in 1911 by Menzies and Dutt [2] who showed that a simple eutectic existed in this system at 210°C for 60 mol % $(\text{KNO}_3)_2$ and 40 mol % $\text{Ca}(\text{NO}_3)_2$. In 1930, A.P. Rostkovski subjected this system, anew, to a very careful investigation. Working with the visual polythermal method, the author showed the existence in the system of the chemical compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$, which incongruently melted at 174°C. The eutectic temperature, being the intersection of the melting point curve for this compound with calcium nitrate, was 145°C with the composition of 49 mo. % of $(\text{KNO}_3)_2$ and 51 mol % of $\text{Ca}(\text{NO}_3)_2$.

Rostkovski noted that the melt in the middle portion hardened into a glass-like mass and could remain in such a condition for several days, this situation resulting from a slow equilibrium fixation. The melt, in composition close to that of the eutectic, formed a thick, viscous mass up to the crystallization point. Crystallization could only be obtained by seeding and with continuous, vigorous agitation. Menzies and Dutt, who studied this system using heating curves plotted with a small number of points naturally could not observe all the above characteristics of the system, and could not testify to the existence of a compound.

Table 1
Binary System $(\text{KNO}_3)_2 - \text{K}_2\text{CrO}_4$

Melt number	Mol % K_2CrO_4	Average crystallization temperature
1	0	336
2	1.0	325
3	2.0	345
4	3.0	364
5	4.0	383
6	6.0	414
7	9.0	444

Table 2
Binary System $\text{Ca}(\text{NO}_3)_2 - \text{CaCrO}_4$

Melt number	Mol % CaCrO_4	Average crystallization temperature
1	0	527
2	1.0	524
3	1.5	520
4	2.0	516
5	2.5	512
6	3.0	520
7	4.0	534

We studied several points of this system and in all cases obtained very good agreement with the data of A.P. Rostkovski. The heating curves which we prepared for compositions close to the eutectic, and which were conducted using Engineer Simonov's pyrometer, indicated the existence of a eutectic point at a temperature of 142°C.

2. Binary System $(\text{KNO}_3)_2 - \text{K}_2\text{CrO}_4$

First studied by Guthrie [3]. He found the eutectic point at 295°C and 2 mol % of K_2CrO_4 . The eutectic temperature which we established is quite higher, that is 321°C and 1.5 mol % of K_2CrO_4 . Guthrie's data coincides quite well with ours. The divergence in the determination of the eutectic temperature can be explained by the melting point of potassium nitrate, which was determined by Guthrie as 320°C (Table 1, Diagram 1).

3. Binary System $\text{Ca}(\text{NO}_3)_2 - \text{CaCrO}_4$

Studied by us. Here we have a eutectic at 512°C and 2.5 mol % of CaCrO_4 (Table 2, Diagram 2).

DIAGONAL CROSS-SECTIONS

1. Stable Diagonal $(\text{KNO}_3)_2 - \text{CaCrO}_4$

The potassium nitrate branch is very short and drops steeply to the eutectic point, situated at a temperature of 317°C and 0.75 mol % of CaCrO_4 (Table 3, Diagram 3).

2. Metastable Diagonal $\text{Ca}(\text{NO}_3)_2 - \text{K}_2\text{CrO}_4$

The metastable diagonal, resulting from the decomposition of calcium nitrate, can only be studied at 530°C . The eutectic point -- the intersection of the branches for the crystallization of calcium nitrate with the product of the double decomposition reaction CaCrO_4 -- is situated at 506°C and 1.5 mol % of K_2CrO_4 (Table 4, Diagram 4).

Table 3

Stable Diagonal $(\text{KNO}_3)_2 - \text{CaCrO}_4$

Melt number	mol % CaCrO_4	Average crystallization temperature
1	0	336
2	0.5	324
3	1.0	416
4	2.0	440

Table 4

Metastable Diagonal $\text{Ca}(\text{NO}_3)_2 - \text{K}_2\text{CrO}_4$

Melt number	mol % K_2CrO_4	Average crystallization temperature
1	0	527
2	0.5	522
3	1.0	517
4	1.5	508
5	2.0	518
6	2.5	530

DIAGONALS OF TRINARY SYSTEMS

To clarify the question of the nature, position and magnitude of the regions, 7 internal trinary cross-sections were investigated. All the cross-sections can be conveniently examined by dividing them into two series.

1st Series. Cross-sections Nos. 1, 2, 3, 4, 5.

All the cross-sections of this series originate from the lateral sides, pertaining to potassium and calcium nitrates and are directed toward the potassium chromate side; all of these consist of two branches. The five branches pertaining to the nitrates are slightly slanted and very short, occupying in all, several hundredths of a percent. Therefore, to conveniently read the figures we had to enlarge the scale 50 times. The second branch of these cross sections pertain to calcium chromate, whose region occupies almost an entire quadrant of the system.

Cross-section No. 1 $[25.0\% (\text{KNO}_3)_2 + 75.0\% \text{Ca}(\text{NO}_3)_2] \rightarrow \text{K}_2\text{CrO}_4$

The branch for the separation of the first calcium nitrate crystals intersects the branch pertaining to calcium chromate at 392°C and 0.12% K_2CrO_4 (Table 5, Diagram 5).

Cross section No. 2 $[45.0\% (\text{KNO}_3)_2 + 55.0\% \text{Ca}(\text{NO}_3)_2] \rightarrow \text{K}_2\text{CrO}_4$

The intersection of the $\text{Ca}(\text{NO}_3)_2$ and CaCrO_4 branches takes place at 183°C and 0.05 mol % of K_2CrO_4 (Table 6, Diagram 5).

Cross section No. 3 $[51.0\% \text{Ca}(\text{NO}_3)_2 + 49.0\% (\text{KNO}_3)_2] \rightarrow \text{K}_2\text{CrO}_4$

Cross-section No. 3 originates from the eutectic point of the binary system $(\text{KNO}_3)_2 - \text{Ca}(\text{NO}_3)_2$. The principal purpose of the cross section is to study the permissible mixture of chromates at the eutectic $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2$, which would not increase the melting point. The eutectic point of the given cross section is situated at 140°C and 0.03 mol % of K_2CrO_4 . Upon introducing another 0.01% K_2CrO_4 into the melt, the temperature is raised to 226°C , and at a concentration of 0.05 mol % of the chromate the first crystals are observed to separate at 370°C (Table 7, Diagram 5).

Cross-Section No. 4 $[60.0\% (\text{KNO}_3)_2 + 40.0\% \text{Ca}(\text{NO}_3)_2] \rightarrow \text{K}_2\text{CrO}_4$

The diagram consists of two branches. The melting-point curves of potassium nitrate

and calcium chromate intersect at 192°C and 0.03 mol % K_2CrO_4 (Table 7, Diagram 5).

Table 5
Cross Section No. 1

Melt number	Mol % K_2CrO_4	Average crystallization temperature
1	0	398
2	0.05	396
3	0.1	394
4	0.12	400
5	0.15	460

Table 6
Cross Section No. 2

Melt number	Mol % K_2CrO_4	Average crystallization temperature
1	0	196
2	0.03	194
3	0.05	255
4	0.06	440

Cross-Section No. 5 $[25.0\% Ca(NO_3)_2 + 75.0\% (KNO_3)_2] \rightarrow K_2CrO_4$

The curves pertaining to $(KNO_3)_2$ and $CaCrO_4$ intersect at 265°C and 0.07% K_2CrO_4 .

Table 7
Cross Section No. 3

Melt No.	Mol % K_2CrO_4	Ave. crystallization temperature
1	0	142
2	0.01	141.5
3	0.02	141
4	0.03	141
5	0.04	226
6	0.05	370

Table 8
Cross Section No. 4

Melt No.	Mol % K_2CrO_4	Ave. crystallization temperature
1	0	193
2	0.03	192
3	0.05	340
4	0.06	434

Table 9
Cross Section No. 5

Melt No.	Mol % K_2CrO_4	Ave. crystallization temperature
1	0	268
2	0.03	267
3	0.06	266
4	0.1	354
5	0.15	481

2nd Series. Cross sections Nos. 6 and 7

The second series of cross sections have as their purpose the explanation of the coincident crystallization lines of potassium and calcium chromates, and the positions of those ternary points where the $(KNO_3)_2$, $CaCrO_4$ and K_2CrO_4 regions converge. The presence of the above ternary points and the direction of the coincident crystallization lines permit the drawing of the conclusion that there is no isomorphism for the calcium and potassium chromates and that the eutectic point of the binary system K_2CrO_4 - $CaCrO_4$ is situated close to potassium chromate.

Cross section No. 6 $[97.0\% (KNO_3)_2 + 3.0\% K_2CrO_4] \rightarrow Ca(NO_3)_2$

The diagram has two branches. The potassium chromate branch intersects the curve where the first crystals of $CaCrO_4$ separate out, at 356°C and 0.32 mol % of $Ca(NO_3)_2$ (Table 10, Diagram 6).

Cross section No. 7 $[95.0\% (KNO_3)_2 + 5.0\% K_2CrO_4] \rightarrow Ca(NO_3)_2$

The diagram is analogous to the previous one. The intersection of the branches takes place at 388°C and 0.40% $Ca(NO_3)_2$. (Table 11, Diagram 6).

Examining the quadrant for the system as a whole, we see that almost the entire diagram is occupied by the calcium chromate region, which is the most refractory component. The system has three nonvariant points - A, B and C. The temperature of the ternary points can be visualized as crystallization projections of the system on the lateral side $(KNO_3)_2$ - $Ca(NO_3)_2$ (Diagram 8).

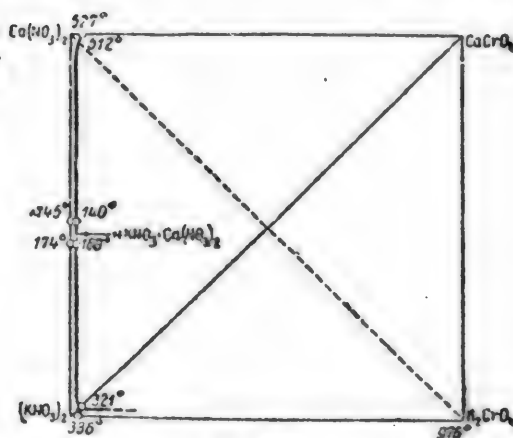
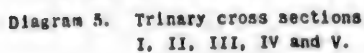
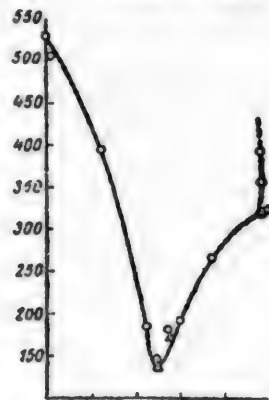
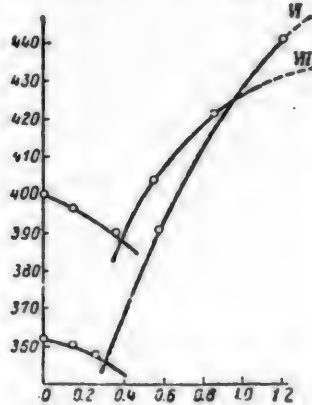
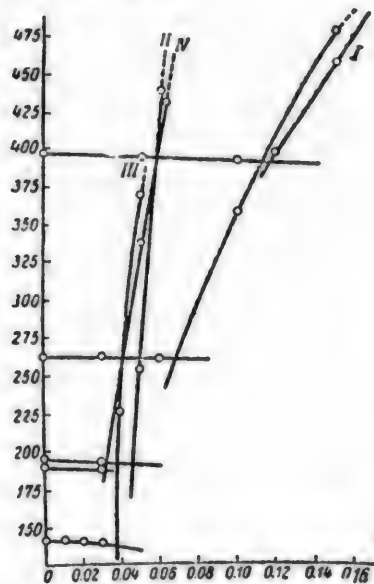
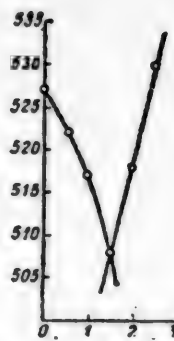
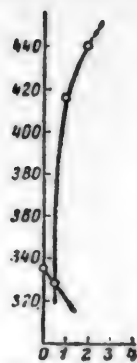
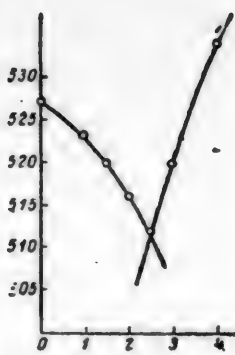
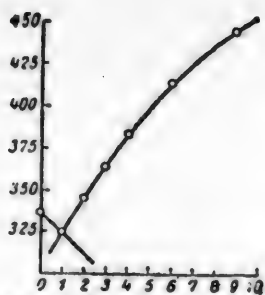


Table 10
Cross Section No. 6

Melt No.	Mol % $\text{Ca}(\text{NO}_3)_2$	Average crystallization temperature
1	0	362
2	0.14	361
3	0.26	358
4	0.59	390
5	1.23	440

Table 11
Cross Section No. 7

Melt No.	Mol % $\text{Ca}(\text{NO}_3)_2$	Average crystallization temperature
1	0	400
2	0.15	396
3	0.37	390
4	0.56	404
5	0.87	421

Table 12
Composition of the Liquid Phases and Temperature of the Non-variant Points of the System $\text{K}^+, \text{Ca}^{++} \parallel \text{NO}_3^-, \text{CrO}_4^{--}$

Trinary Points	Composition of the Liquid Phase	Temperature	Solid Phase
A	49.00% $(\text{KNO}_3)_2$ + 50.97% $\text{Ca}(\text{NO}_3)_2$ + 0.03% K_2CrO_4	140°C	$\text{Ca}(\text{NO}_3)_2$ + 4 KNO_3 $\text{Ca}(\text{NO}_3)_2$ + CaCrO_4
B	55.47% $(\text{KNO}_3)_2$ + 44.50% $\text{Ca}(\text{NO}_3)_2$ + 0.03% K_2CrO_4	168°C	4 KNO_3 $\text{Ca}(\text{NO}_3)_2$ + CaCrO_4 + KNO_3
C	98.37% $(\text{KNO}_3)_2$ + 1.38% K_2CrO_4 + 0.25% $\text{Ca}(\text{NO}_3)_2$	319°C	KNO_3 + CaCrO_4 + K_2CrO_4

CONCLUSIONS

1. The mutually irreversible system of the nitrates and chromates of potassium and calcium was studied at a temperature interval from 140 to 530°C.
2. New experimental confirmation was obtained of the position taken by Prof. A.P. Palkin who introduced the principal that in phase systems the direction of the reaction moves towards the side containing the most refractory component.
3. On the basis of the diagram study a mutual system for use as a heating medium may be presented with the following composition: $(\text{KNO}_3)_2$ - 49.00 mol %, $\text{Ca}(\text{NO}_3)_2$ - 50.97 mol %, K_2CrO_4 - 0.03 mol %

The given heating medium melts at 140°C and is completely stable at temperatures up to 520°C. From 180 to 190°C the melt exhibits a viscous character, but when the temperature is raised the viscosity quickly drops, and at 200°C the melt becomes an easily mobile liquid.

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POROUS STRUCTURE OF CATALYSTS -- CATALYTIC ACTIVITY

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A heterogeneous catalytic reaction is characterized by its rate being a function of the surface contact of the reacting materials [1]. Neglecting the action of the catalyst, the activity is proportional to the specific surface. The physical and chemical state of the surface has not been considered in this paper; it is assumed that the properties of the surface are identical in all cases.

The catalysts investigated were prepared from silica gel and activated with aluminum oxide. The surface of the silica gel carrier is developed at the expense of the pores formed at the moment of coagulation of the sol of silicic acid. It is of interest to compare the activity of these catalysts with their porosity and with the distribution of pores in a given volume, i.e. to obtain structural curves; this serves to characterize the extent of the inner surface of the catalyst.

Of considerable importance, however, is the accessibility of the effective structural surface of the carrier to the gaseous molecules of the reacting product. The latter in our case represents a mixture of heavy hydrocarbons, boiling range $200-400^{\circ}$, and with a mean cross sectional molecular radius of approximately 5 - 7 Å.

In considering the phenomena associated with the ultra porosity of sorbents [2], [3], it may be possible that in the catalytic cracking of heavy hydrocarbons, the active surface consists of only that portion composed of pores with radii larger than the dimensions of the hydrocarbon molecules.

The present investigation was confined to an investigation of the approximate radii of pores, by using Tomson's formula for capillary condensation as modified by Zsigmondy [4].

The finer the porosity, the more inaccurate is this formula since the adsorbed layer of liquid greatly distorts the actual radius of the capillary. In comparative experiments, however, this is of but minor importance.

EXPERIMENTAL

A vacuum apparatus was used for the experiments. The measurements of the absorption of water vapors were made by using a manometric method. The most convenient manometer for accurate measurements of equilibrium vapor pressures was the inclined type of Huggins. This was filled with tetralin while at the same time evacuating the gas to a pressure equal to the saturated vapors of this liquid.

One mm. of the scale graduation of the manometer corresponded to 0.0183 mm. mercury.

The catalyst, 10 g., was placed in a Pyrex flask (Fig. 1), which was evacuated for 8 - 10 hours at 500° . When the pressure read on a McLeod gage reached $1 \cdot 10^{-5}$ mm.Hg, the evacuation was halted and the flask was cooled to room temperature using a thermostat; the temperature was maintained at 18.7° . All experiments were carried out at this temperature.

The following procedure was followed: The water vapors were introduced into the evacuated apparatus up to 700 - 800 mm. on the Huggins manometer (15 - 16 mm. Hg): after opening stopcock K_1 , the water vapors were absorbed by the catalyst. The equilibrium pressure was recorded, and again, with stopcock K_1 closed, the pressure was brought up to 700 - 800 mm. This was repeated until the catalyst was completely saturated. From the difference between the initial and equilibrium pressures, the amount of liquid condensed in the pores of the catalyst was calculated.

In order to obtain characteristic curves, the following ratios were taken: V/V_S , i.e., the ratio of the volume of adsorbed liquid in capillaries of radii less than or at equilibrium pressure of vapors (p) over the catalyst to the entire volume of the slanting space of the catalyst at a pressure of saturated vapor (p_S) over the plane surface at 18.7°C.

The seven catalysts used in the experiments were prepared from water glass with a varying modulus and degree of washing of the gel; they were activated under the same conditions by means of a 3% solution of aluminum sulfate.

Table I presents the working characteristics of these catalysts. The catalytic activity is given in terms of a percentage yield of benzene with the upper boiling point of distillate in the cracking of gas oil at 200°C.

The structural curves, the porosity and average pore size were determined for these catalysts: They were plotted on one graph for ease of comparison (Figure 3).

Apparently, a decrease in the radii of the pores while maintaining the same unit porosity (volume of pores in one cm^3 gel) should result in an increase in surface with a corresponding increase in the activity of the catalyst. However, as pointed out, the effect of ultra porosity of gels may lead to a reversal of activity, i.e. to a decrease in the case of a highly porous catalyst. This effect was actually observed.

The activity of catalysts was found to depend on the structure of the carrier, i.e., in the region 9 - 10 Å the catalysts showed a well defined maximum catalytic activity.

This is clearly illustrated in the curve given in Fig. 3.

The average size of the molecules of reacting vapor can be used for an approximate calculation of the accessible volume of pores for these molecules (effective porosity - P_{eff} . catalyst). If we represent the unit porosity as (P) then:

$$P_{\text{eff.}} = P(1 - \frac{V_u}{V_S}) \quad (1)$$

where $\frac{V_u}{V_S}$ - is the coefficient of ultra porosity; the latter is determined from the structural curve with the radii of pores smaller than the average dimensions of approaching molecules: V_u - volume of ultra pores.

The values of unit porosity and calculated values of effective porosity per unit volume of catalyst are given in Table 2.

As shown in the table, the activity is proportional only to the value of the accessible surface of the catalyst. Therefore the specific activity (the activity in % referred to a unit of accessible surface) was found to be in most cases almost equal, on the whole:

$$A = \frac{K}{S_{\text{eff.}}} \approx 0.1.$$

The area is approximate. Calculations were made with the assumption that the pores of the catalyst are cylindrical, and equal to the average radius. The following relation was used:

$$S_{\text{eff.}} = \frac{2 P_{\text{eff.}}}{r} \quad (2)$$

where r - the average radius of pores in a given volume of catalyst.

ACTIVATION OF SILICA GEL

The data for the chemical analyses of the content of activator per cm^3 of silica gel are given in Table 3.

In general, the adsorption of aluminum ions from solutions of aluminum salts depends on the size of surface. It is true that no strict proportionality can be expected in this case; nevertheless it can be shown that the amount of aluminum oxide available on the surface is entirely insufficient for the covering of silica gel with a compact monomolecular layer.

On the average 0.04 g. of aluminum oxide is used for a surface of 800 m^2 . With the radius of the Al_2O_3 molecule equal to 2.5 \AA , the area, taken up by 0.04 g will be equal:

$$S_{\text{Al}_2\text{O}_3} = \frac{6.06 \cdot 10^{23} \cdot 0.04 \cdot 25 \cdot 10^{-16}}{101.9} = 5.9 \cdot 10^5 \text{ cm}^2$$

This would be only 7.5% of the total surface:

$$\alpha = \frac{S_{\text{Al}_2\text{O}_3}}{S} = \frac{5.9 \cdot 100}{800} \approx 7.5\%$$

Naturally it was assumed that an increase in the degree of filling of the surface with aluminum oxide would increase to some extent the number of active points. However, it was found that a further increase in the concentration of the salt in solution did not lead to an increase in the activity of the catalyst; in some cases this resulted in a decrease. Hence a detailed study of the activation process of silica gel was undertaken.

Since the silicic acid gel is activated by a solution of aluminum salt after being coagulated and washed, we apparently have a case of absorption of aluminum by the sorbent. It is known that silica gel is an electronegative adsorbent and therefore adsorbs only cations from solutions. The adsorption from solution of electrolytes can take place either by exchange or hydrolysis or both. In both instances, hydrogen would accumulate in solution. The increase in concentration of hydrogen ions after activation with aluminum sulfate was established experimentally. The pH of the solution was determined after a 2 hour period of activation at a temperature of 80° . The change in hydrogen ion concentration was from $2.5 \cdot 10^{-4}$ mole/liter to $8 \cdot 10^{-3}$ mole/liter. This represents a more than 30-fold increase. Hence, it follows that silica gel in a solution of aluminum sulfate shifts the equilibrium towards the formation of hydrogen ions, but the accumulation of the latter in solution results in a reversed process of solution of the aluminum oxide formed. In this case, of course, it is impossible to attain a complete coverage of the surface of silica gel with the cations of the

*) This investigation was carried out mainly in 1940-1 and was interrupted during the war; recently in this laboratory and also in the MGU adsorption laboratory some of these areas were again measured and calculated by recent methods [8]. For sample GEL the average radius was 10 \AA , total area $725 \text{ m}^2/\text{cm}^3$ (compare with Table 2).

The authors welcome this opportunity to acknowledge the aid of A.V. Kiselev, Prof. at Moscow University, for the measurements carried out in his laboratory, and for his valuable suggestions.

salt from the solution. Hence it follows also that in the case of adsorption of salts of stronger acids, saturation of the adsorbing forces of the surface would occur very much before there was full coverage with solution cations.

It is known [7], [8], that in the case of hydrolytic adsorption the cations of the salts of weak acids are adsorbed more readily than those of stronger acids, since in most cases they are hydrolyzed. This is in complete agreement with our concepts and is confirmed by experiment (Table 4).

Aluminum salts of both weak and strong acids were taken in the same molar concentration (0.1 molar) with respect to Al_2O_3 . The adsorption was continued for 2 hours at room temperature and then the residual amount of Al_2O_3 in No. 1 and No. 2 solutions was determined.

As shown in the table, adsorption of the oxide is 8 times greater from the solution of a salt of the less dissociated acid.

The effect of cracking upon catalysts with an increased content of aluminum is given in Fig. 4.

It is apparent that a more complete saturation of the surface of the catalyst by aluminum oxide and a correspondingly higher limit of activity takes place for the less dissociated salt at lower concentrations of this salt in solution.

On the average, results on the determination of activity in catalysts with an increased content of aluminum were 25% higher than those obtained using the sulfate as activator.

DISCUSSION OF RESULTS

Since the activity is expressed by the equation:

$$K = A \cdot S_{\text{eff.}}$$

and from expression (1) it follows that:

$$K = A \cdot \frac{2P_{\text{eff}}}{r}$$

then by using (1), we obtain:

$$K = A \cdot \frac{2P}{r} - \left(1 - \frac{V_u}{V_s}\right). \quad (3)$$

This equation refers to the curve (Fig. 3), since the coefficient of ultraporosity is a function of the distribution of pores according to their dimensions. From equation (3) it follows that the best catalyst with reference to its activity is the one which has the largest surface accessible to the molecules of the approaching substance; i.e., the one that has the most abrupt characteristics in the region of the 'accessible' cross section of pores.

The porous structure of the catalyst influences not only the absolute yields of the product, but also its chemical composition. In the investigation of aluminum silicate catalysts activating the decomposition of Dossorsky gas oil at a temperature of 450° it was discovered that for almost similar yields (based on the raw material, of benzene fractions, the results for the gaseous fractions differed greatly. From many such observations a definite regularity could be derived. This is illustrated in Table 5.

As the data in Table 5 indicates, for catalysts with large pores, the gas formation is less noticeable than in the case of those having fine pores. This suggests that the ultra-pores of the catalyst not only take no part in the principal reaction of decomposition of hydrocarbon molecules, but in addition have an undesirable effect, causing a further decomposition of the "benzene" molecules, which penetrate and are adsorbed by these pores.

In addition the catalysts having fine pores are regenerated with greater difficulty from the

coke deposited on the samples. A noticeable difference was exhibited also by these catalysts with respect to thermal stability. Even heating for a short time at a temperature of 600-650° resulted in a pronounced decrease in activity; this was associated, as shown experimentally, with a decrease of surface in the region of fine pores and pores similar in their dimensions to the molecules of reacting vapor.

Therefore, it may be concluded that in order to obtain a better yield of benzene and thermally stable catalysts with good regenerative properties, the catalysts should be synthesized with a widely developed surface in the region of pores, greater than the effective radii of the reacting molecules; any decrease in the total surface should be compensated for by a marked increase in the aluminum present per unit surface of catalyst. The latter can be achieved by preparing catalysts from mutually precipitated silicoaluminum gels. In this case the amount of aluminum oxide exceeds considerably the previously mentioned limits which were obtained by penetration of the silica gel matrix with a solution of an aluminum salt.

An investigation of the structure and chemical composition of the Houdry catalyst for the fixed bed process indicates that a well defined maximum with respect to distribution of pores according to radii exists; this maximum corresponds to the pores having radii equal to 20 Å, a surface equal to 430 m²/cm³, and a content of aluminum oxide up to 25% per unit volume of catalyst. The published data [9] on the manufacture of catalyst pellets by the Socony Vacuum Co. characterizes its porosity by an average radius of pores equal also to 22 - 25 Å; apparently, this is the optimum for catalysts used in cracking. To obtain this porosity, a number of specific measures are used in the treatment of the gel, including a final annealing of the catalyst at a high temperature.

CONCLUSIONS

1). Measurements have been made of the surface, average size of pores and unit porosity of a series of silica gel catalysts, activated by the same method, namely, penetration with a solution of aluminum sulfate.

2) It has been found that the activity of the catalysts in accelerating decomposition reactions of heavy hydrocarbons is proportional to the surface accessible to the molecules of the reacting product. For the series of catalysts the optimum value for the radius of the pores is in the range of 9 - 10 Å.

3). A study has been made of the activation of silica gel by using aluminum salts. It has been found that the aluminum ions are precipitated on silica gel as a result of a surface chemical reaction, in place of hydrogen ions entering the solution. It has been shown that by substituting in the solution of the activator anions of weak acids in place of anions of strong acids, the limit of aluminum absorption can be raised; also, the catalytic activity is increased somewhat.

4) It has been observed that catalysts of fine porosity give rise in the cracking of gas-oil fractions to a greater gas formation than the catalysts having large pores; they are also regenerated with greater difficulty and are thermally unstable. These phenomena are due to the presence of a large number of ultrapores in the volume of the catalyst.

5) It has been found convenient to synthesize aluminosilicate catalysts with a widely developed porosity in the range of uniform dimensions of the reacting molecules; any slight decrease in the total surface is compensated by an increase in the amount of aluminum oxide added.

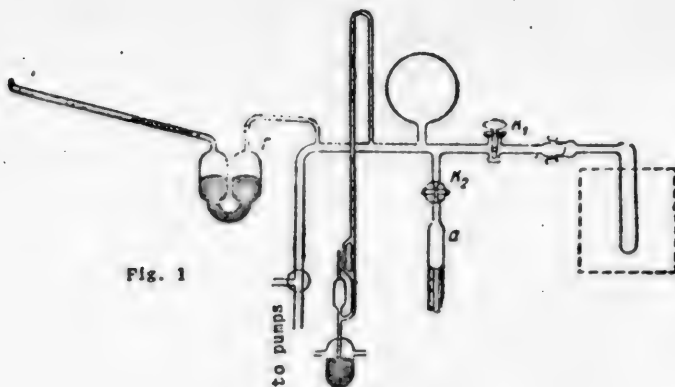


Fig. 1

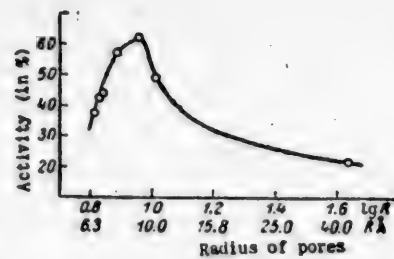


Fig. 3

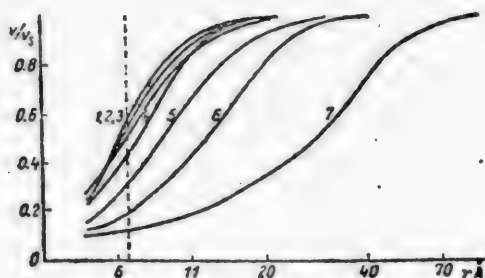


Fig. 2. Characteristic Curves for Aluminosilicate

Catalysts Used in Cracking
2 - 301; 2 - 1 MA-8; 3 - 106; 4 - 56L;
5 - 64L; 6 - 2NC; 7 - 1 MA-1. (The
broken line separates the working volume
of pores from ultrapores for the given
reaction.)

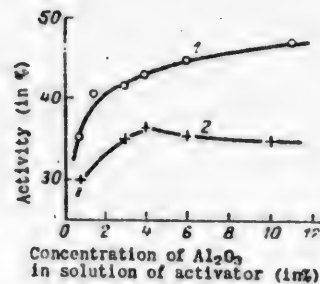


Fig. 4. Catalytic activity of silica gel, activated by solutions of salts of weak and strong acids, as a function of the concentration of Al_2O_3 in solution. 1 - activator, solution of aluminum acetate. 2 - activator, solution of aluminum sulfate.

Table 1

Name of Catalyst	Activity K (in %)	Ratio in water glass $Na_2O:SiO_2$	Specific gravity of water glass	In prep. of catalyst, gel is washed with H_2O	
				Cold	hot
64 L	62.0	3.1	1.15	3 times	14 times
56 L	57.5	3.1	1.15	5	3
2 NC 5	43.0	2.9	1.45	5	3
1 MA-8	43.5	2.9	1.2	5	3
106	42.0	3.1	1.2	5	3
301	37.0	3.1	1.2	5	3
1 MA-1	22.5	2.9	1.2	5	2)

Table 2

Name of catalyst	Total activity (in %)	Unit porosity (in %)	Av. radius of pores (approx.)	Total surface in m^2/cm^3	Coefficient of ultra-porosity ($\frac{r_p}{r_m}$)	Pores of radius $> r_p$	Accessible surface in m^2/cm^3	Activity per unit of surface A
61 L . . .	62.0	35.8	9.0	795	0.31	24.7	550	0.113
56 L . . .	57.5	30.2	7.6	800	0.42	17.5	460	0.125
2 NC-5 . .	49.0	40.0	12.6	635	0.20	32.0	510	0.097
1 MA-8 . .	43.5	24.5	6.9	710	0.51	12.0	350	0.125
106 . . .	42.0	29.6	6.7	883	0.52	14.2	425	0.100
301 . . .	37.0	30.0	6.5	930	0.57	12.9	400	0.093
1 MA-1 . .	22.5	43.8	44.0	205	0.07	42.3	190	0.118

Table 3

Nature of Catalyst	% Al_2O_3 per 1cm ³	Total surface silica gel (in m^2/cm^3)	% Al_2O_3 S $\cdot 10^{-8}$
61 L	3.72	795	4.7
56 L	3.94	800	4.5
2 NC-5	2.75	635	4.3
1 MA-8	2.87	710	4.0
106	4.05	880	4.5
301	3.75	930	4.1
1 MA-1	0.80	205	5.9

Table 4

Solution of Activator	No. 1: $Al(CH_3COO)_3$	No. 2: $Al(NO_3)_3$
wt. silica gel, g.	50	50
Concentration, moles/liter		
before adsorption . . .	0.0956	0.0952
after adsorption . . .	0.0408	0.0894
adsorbed	0.0548	0.0058

Table 5

Name of Catalyst	Yield of Benzene (wt. %)	Yield of gas (wt. %)	Structure	Weight of Catalyst
1 MA-2	37.0	6.3	Large pores	0.348
1 MA-3	36.6	21.2	Small pores	0.659
1 MA-33	34.4	18.7	Small pores	0.707
1 MA-40	33.0	8.4	Large pores	0.453

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DOUBLE HALOGENIDES OF ARSENIC AND ORGANIC BASES

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Double halogenides of antimony and bismuth with organic bases exist in large numbers, but similar derivatives of arsenic have been but little investigated. A series of new complexes have been obtained, clarifying to a certain extent questions as to the structure of these compounds; several interesting properties of complex formation have also been noted.

The complexes obtained to date in our laboratory are listed in Table 1.

All of these compounds, and also the double halogenides of antimony and bismuth with organic and inorganic halogen salts reported in the literature can be divided into 6 main groups; these differ by the ratio of the number of molecules of initial substances (RHX and MX_3) to those entering into the composition of the complexes (for monoacidic bases and monovalent metals). The given ratios are: 3:1, 5:2, 2:1, 3:2, 1:1 and 1:2 (see Table 2).

Complexes of this type are obtained by interaction of initial substances dissolved in suitable organic and inorganic solvents. As solvents, hydrogen halide acids were generally used. Organic solvents used were: acetone, fatty acids, diethyl ether and, in our experiments, chloroform. All complexes were formed as crystalline precipitates which in most cases hydrolyzed when dissolved in water, yielding acid solutions.

The composition of the complexes depends upon the nature of the applied solvent, the relative amounts of starting materials, the order of decanting of solutions, and the temperature. This dependency for the derivatives of $BiCl_3$ was indicated by Gutbier and Miller [2]. This was also observed in our laboratory for the derivatives of arsenic halides. An interesting property of the latter was also noted, i.e., the ability of some complexes under certain conditions to be transformed into another form. Such transformations have been most completely observed in the derivatives of pyridinehydrobromide.

A condensation of this salt with $AsBr_3$ yields complexes of four different groups.

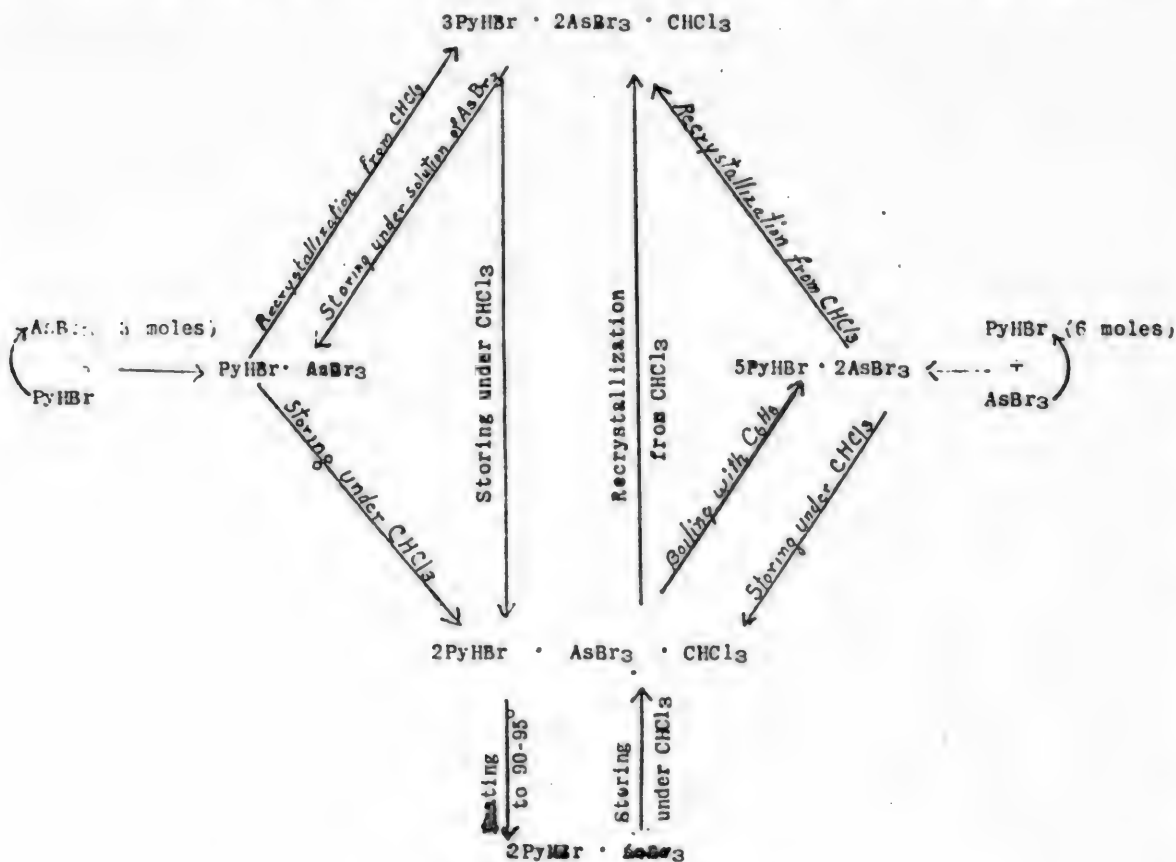
Condensation of $PyHCl$ and $PyHI$ with the corresponding arsenic halides each yielded only two compounds. The following data have been obtained for the conditions governing the formation and mutual transformations for the derivatives of $PyHBr$ and $AsBr_3$.

The reaction of $PyHBr$ with an excess of $AsBr_3$ (3 moles) yields a complex $PyHBr \cdot AsBr_3$ in prism-like crystals (m.p. $127^\circ C$). Recrystallization of this compound from the mother liquor yields initially white needles of the composition $3PyHBr \cdot 2AsBr_3 \cdot CHCl_3$ (m.p. $124^\circ C$). When this complex is stored under the initial solution for 2 - 3 days at room temperature, a completely reversible transformation to $PyHBr \cdot AsBr_3$ takes place. When these two complexes taken separately are placed in pure chloroform, a new form -- $2PyHBr \cdot AsBr_3 \cdot CHCl_3$, in yellow needles (m.p. 144°) is formed after a few days.

The drying of $2PyHBr \cdot AsBr_3 \cdot CHCl_3$ in vacuo on a boiling water bath, results in

the loss of the crystallized chloroform, a white powder at m.p. 156°C of composition $2\text{PyHBr} \cdot \text{AsBr}_3$ is obtained. Storing the latter under chloroform yields the initial form -- $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$. Boiling $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$ with chloroform discolors the compound close to the boiling point of chloroform (this also occurs when the dry preparation is heated). When cooled, a complex $3\text{PyHBr} \cdot 2\text{AsBr}_3 \cdot \text{CHCl}_3$ is precipitated.

On the addition of AsBr_3 solution to a hot solution of PyHBr (6 moles) another compound - $5\text{PyHBr} \cdot 2\text{AsBr}_3$ in yellow leaves (m.p. 163°C) is formed. The complex is less soluble in CHCl_3 than the other Br-containing forms. Storing $5\text{PyHBr} \cdot 2\text{AsBr}_3$ under pure CHCl_3 results in the formation of $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$. When boiled with CHCl_3 white needles of $3\text{PyHBr} \cdot 2\text{AsBr}_3 \cdot \text{CHCl}_3$ are separated, ~~which rapidly~~ (after 2 - 3 hours at room temperature) are transformed to $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$. Boiling $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$ with benzene yields a residue of composition $5\text{PyHBr} \cdot \text{AsBr}_3$. On the basis of the data the form $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot \text{CHCl}_3$ should be considered as the most stable at room temperature. All transformations of Br-containing complexes can be expressed by the following diagram.



For derivatives of PyHCl and AsCl_3 we have the following:

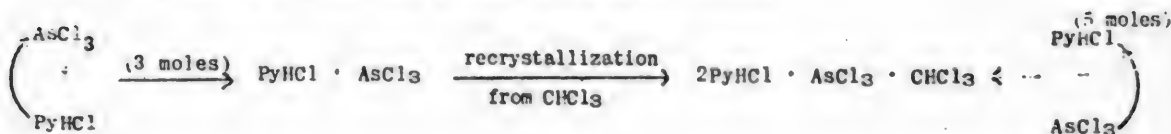
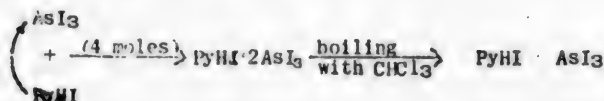


Table 1

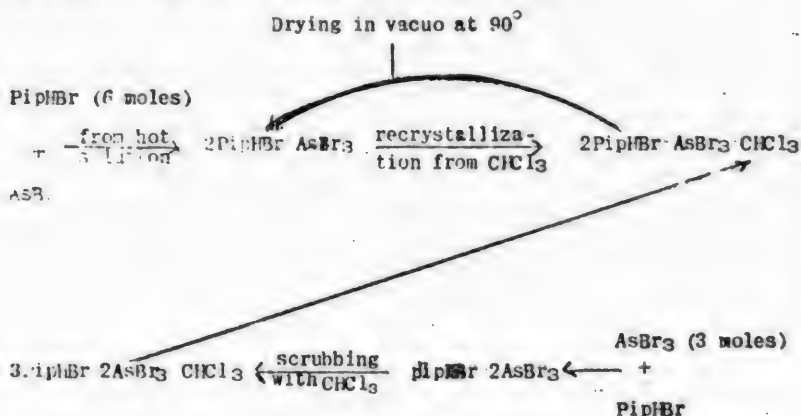
Analytical composition	Melting point	Color and form of crystals
Complexes of the salts of pyridine and its derivatives (Py = C ₅ H ₅ N)		
1 2PyHCl · AsCl ₃ · CHCl ₃	125°C	Fine, colorless needles
2 PyHCl · AsCl ₃	114	colorless needles
3 5PyHBr · 2AsBr ₃	163	colorless, heavy rhombic plates
4 2PyHBr · AsBr ₃ · CHCl ₃	144	yellow prisms
5 2PyHBr · AsBr ₃	156	light yellow powder
6 3PyHBr · 2AsBr ₃ · CHCl ₃	124	long, thin, colorless needles
7 PyHBr · AsBr ₃	127	light yellow prisms
8 3α-PicolinHBr · 2AsBr ₃	100	yellow rhombic plates
9 α-PicHBr · AsBr ₃	65	colorless plates
10 2β-PicHBr · AsBr ₃	136	light yellow rhombic plates
11 β-PicHBr · AsBr ₃	63	light yellow rhombic plates
12 2PyC ₂ H ₅ Br · AsBr ₃	--	light yellow needles
13 3PyC ₄ H ₉ Br · 2AsBr ₃ · CHCl ₃	70	light yellow prism-like needles
14 PyC ₃ H ₇ Br · AsBr ₃	112	colorless plates
15 PyHI · AsI ₃	decomposes	fine orange prism-like needles
16 PyHI · 2AsI ₃	decomposes	brick-red fine prisms
Complexes of the salts of quinoline and its derivatives (QH = C ₉ H ₇ N)		
17 QHCl · AsCl ₃	123	Fine, colorless needles
18 2QHBr · AsBr ₃	138	yellow prisms
19 QHBr · AsBr ₃	151	greenish-yellow square prisms
20 2QC ₂ H ₅ Br · AsBr ₃	182	greenish-yellow crystals
21 QC ₂ H ₅ Br · AsBr ₃	131	yellow, bipyramidal hexahedral prisms
22 QC ₂ H ₅ Br · 2AsBr ₃	97	light yellow plates
23 QC ₄ H ₉ Br · AsBr ₃	78	light yellow needles
24 QHI · AsI ₃	decomposes	golden leaves
25 QHI · 2AsI ₃	decomposes	orange rhombic plates
Complexes of the salts of piperidine (Pip = C ₆ H ₁₁ N)		
26 2PipHCl · AsCl ₃ · CHCl ₃	134	colorless needles
27 3PipHCl · 2AsCl ₃ · CHCl ₃	130	colorless leaves
28 2PipHBr · AsBr ₃	179	hexahedral prisms
29 2PipHBr · AsBr ₃ · CHCl ₃	174	light green, long needles
30 3PipHBr · 2AsBr ₃ · CHCl ₃	-	thin, colorless needles
31 PipHBr · 2AsBr ₃	-	light, greenish-yellow prisms
32 2PipHI · AsI ₃ · CHCl ₃	148 with decomp.	red needles

Remarks: The melting point of complexes containing chloroform was determined in closed capillaries. The complexes melt over a range of several degrees. In the table are listed the temperatures at the completion of melting.

For derivatives of PyHI and AsI₃ the corresponding scheme can be expressed as:



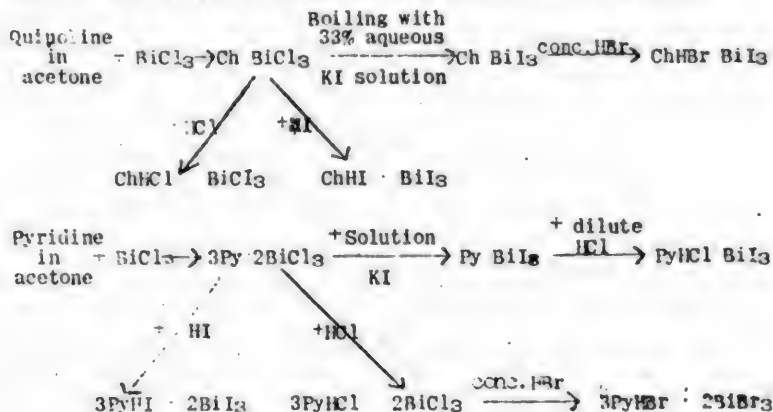
Interesting results are obtained for the system piperidine HBr-AsBr₃. They can be expressed by the scheme:



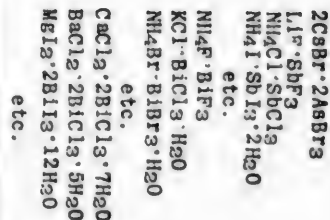
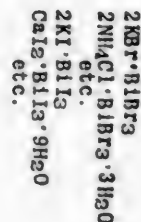
PipHBr · 2AsBr₃ is stable only under a fairly concentrated solution of AsBr₃.

For the system α-picoline HBr-AsBr₃, two forms were obtained. PicHBr · AsBr₃ and 3PicHBr · 2AsBr₃. β-Picoline HBr and AsBr₃ yielded 2PicHBr · AsBr₃ and PicHBr · AsBr₃. For the system CH₃-AsBr₃ we have to date only two forms: CH₃HBr · AsBr₃ and 2CH₃HBr · AsBr₃. Of all quinoline complexes investigated in this laboratory, the form ChHX · AsX₃ was found to be the most stable.

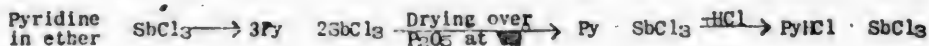
Comparatively little has been published on the mutual transformations of the antimony and bismuth complexes. So, from the work by Hauser, Vanino [7, 10-12], the following schemes can be presented for the derivatives of bismuth.



Inorganic complexes are given in Mellor's monograph [24]



The transformations of SbCl_3 derivatives can be expressed by the following scheme (from the work by Pfeiffer, Schneider [4]).



On the basis of our experimental and literature data, the following conclusions may be drawn.

Note. To conserve space, wherever possible, the composition of the complex compounds will be expressed by 3 numbers, showing respectively the number of molecules of the base or its derivative, molecules of As, Sb, or Bi, and, finally, the molecules of solvent. Thus, for $3\text{PyHBr} \cdot 2\text{AsBr}_3 \cdot \text{CHCl}_3$ the designation will be 3:2:1; for $2\text{PyHBr} \cdot \text{AsBr}_3 \cdot 2 \text{ 1 0}$.

The effect of halogen can be shown in the arsenic derivatives of pyridine. Iodo-containing complexes refer only to the types 1:1:0 and 1:2:0; the form 1:1:0 is the more stable, since it is formed when 1:2:0 is boiled with pure chloroform.

The bromo-containing complexes have a greater number of types: from 5:2:0 to 1:1:0.

The most stable form is 2:1:1. Attempts to obtain a complex 1:2:0 have failed. Such a complex was obtained only in the case of piperidine by adding a solution of PipHBr to an excess, very concentrated solution of AsBr_3 . While attempting to wash this free from the mother liquor by use of chloroform, these crystals were suddenly transformed to a voluminous mass of light, colorless, thin needles of the composition 3:2:1.

For chloro-containing complexes of pyridine (2:1:1 and 1:1:0) the form 1:1:0 appears only in the presence of a considerable excess of AsCl_3 . Recrystallization from chloroform transforms 1:1:0 to 2:1:1, the latter being considered as the more stable.

Thus, with a decrease in the atomic weight of the halogen, the stable forms shift from 1:1:0 to 2:1:1.

Possibly, this shift should be correlated with the decrease in the size of the halogen atoms and, possibly with the decrease of their polarizability in the transition from iodine to chlorine. For the fluoro-containing complexes, the forms 5:2:0 and 3:1:0 can be expected.

The effect of the radical. By substituting quinoline for pyridine, the most stable form independent of the halogen present, is 1:1:0. It is noticeable that the forms 5:3 and 3:2 are missing in the arsenic as well as in the antimony and bismuth complexes. This would suggest that these differences occur because of the larger size of the quinoline ring.

This probably explains the absence of a quinoline complex with crystallized chloroform (screening effect).

Piperidine complexes behave, in general, similar to the pyridine complexes with one exception the form 1:1:0 could not be isolated.

In considering the influence of the basic inorganic atom, (As, Sb, Bi), it should be pointed out that the investigation of the antimony and bismuth complexes was conducted by the earlier research workers under conditions which seldom permitted the preparation of a maximum number of combinations for each pair of initial substances. It had been planned originally to conduct the synthesis of the complexes of As, Sb, and Bi under conditions similar to those used in the preparation of arsenic complexes. For this purpose it was planned to use hydrogen halide acids as the respective solvents. However, the available data permit certain conclusions to be drawn.

Thus, on the whole, for the double halogenides reported, the group 1:1 occurs most often. of almost equal frequency for arsenic is the group 2:1. For BiCl_3 complexes the group 3:1 is most typical. The organic derivatives of SbX_3 have been little investigated, apparently. This also applies to the derivatives of BiF_3 .

Examination of bismuth complexes with individual halogens. The same regularity is encountered as in the case of arsenic: with a decrease in the atomic weight of the halogen, a shift of form occurs from 1:1 to 3:1; however, with bismuth, which has a larger ionic radius than arsenic, the form 3:1 is already present for the chloride.

Structure of the complexes. The role of trivalent arsenic as a complex forming substance requires examination. Arsenic, depending on the nature of the added groups, carries either a negative or a positive charge. A negative charge is found in arsenic where arsenic has complexes similar in nature to those of nitrogen in ammonia. This is confirmed by the presence of such compounds as $2\text{As}(\text{C}_2\text{H}_5)_3 \cdot \text{PtCl}_2$, $4\text{As}(\text{C}_2\text{H}_5)_3 \cdot \text{PtCl}_2$, $\text{As}(\text{C}_2\text{H}_5)_3 \cdot \text{HgCl}_2$ etc. The ability of stibines to form similar complexes is considerably weaker; in bismuthines, it has not been observed at all.

As, Sb, and Bi carry a positive charge in halogen derivatives; here, they can also play the role of an acceptor. This is confirmed by the presence of complexes with halogen salts of piperidine, aliphatic amines, and finally, with halogenides of the alkali metals.

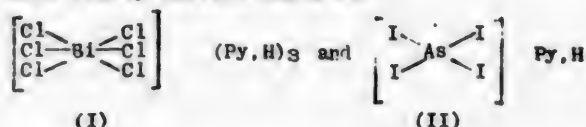
The derivatives of As^{+++} and As^{III} may form complexes with each other. This tetra-ethyl-arsenic iodide forms with AsI_3 $[\text{AsI}_4] \cdot [\text{As}(\text{C}_2\text{H}_5)_4]$ in which the coordination numbers of atoms of arsenic are equal to four.

The elements of subgroups of arsenic may also have a coordination number 6; this is shown by the presence of complexes of the type $3\text{MeX} \cdot \text{SbX}_3$ for halogenides of alkaline metals.

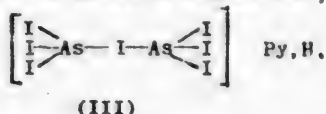
Taking the series 3:1, 5:2, 2:1, 3:2, 1:1 and 1:2 - in which on the left are complexes with the coordination number 6 (type 3:1) and on the right type 1:1 with the coordination number 4, - it is reasonable to assume, that within the series may be complexes with a coordination number 5.

An attempt will be made to present on this basis schemes for the structure of the complexes.

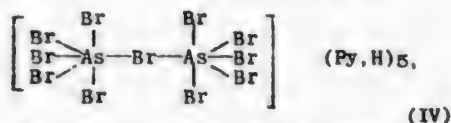
For 3:1 and 1:1 the most likely schemes would be:



For type 1:2, located in the above series to the right of type 1:1, the coordination number can only be 4. The most probable scheme is:



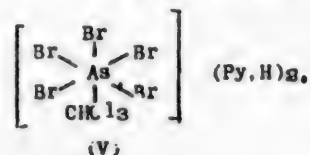
Complex 5:2, located next to 3:1, can be presented as:



The fact that the complex $5\text{PyHBr} \cdot 2\text{AsBr}_3$ is the only one available suggests a fortuitous ratio for the ionic radii of arsenic and bromine and the dimensions of the pyridine ring, giving on the whole a more stable molecule than 3:1.

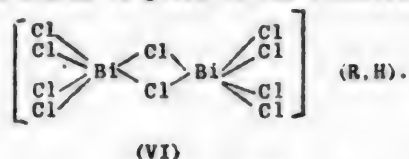
The type 2:1 for our complexes is known in two forms: 2:1:0 and 2:1:1 and, as pointed

out. for PyHBr and PyHCl the last form is the most stable. To this form is ascribed the structure:



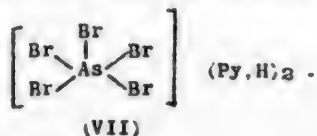
The bond between As and CHCl_3 is quite weak: when heated to 90°C chloroform is split off completely.

For the form 2:1:0 a scheme is given in the literature:



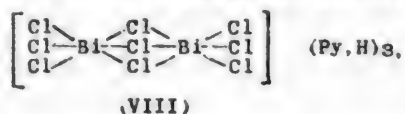
It was suggested by Gutbier and Müller [2] and Dybsky and Wagenhofer [9]. To this form is ascribed a double molecule.

Considering the case of transformation between 2:1:0 and 2:1:1 observed in our experiments, a scheme is considered possible in which the central atom has a coordination number 5:



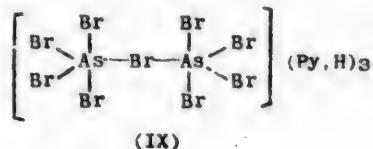
The coordination number 5, while seldom encountered, is possible. A series of compounds are available in which the distribution of five groups around the main nucleus has been proved. Thus, Wells [28] showed by means of x rays that $(\text{CH}_3)_3\text{SbBr}_2$ has a structure of trihedral bipyramids in which the bromine atoms occupy the vertex of the pyramid. Both distances $\text{Sb}-\text{Br}$ are the same and are intermediate between those required for covalent and electrovalent bond (resonance bond). PX_5 and SbCl_5 have a similar structure [27].

To the last type - 3.2, Gutbier and Müller ascribe the structure:

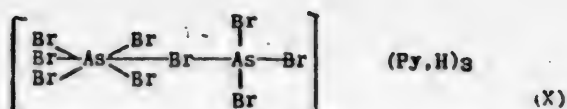


This scheme has 3 four-membered cycles: this hardly seems possible for a fairly stable molecule. The authors of the schemes (VI) and (VIII) give no experimental confirmation and state [2] that they "are forced to base their conclusions as to the constitution of these compounds on analytical data and conclusions derived in analogous cases".

After accepting scheme (VII), it would be quite acceptable to ascribe to the type 3.2 the structure.

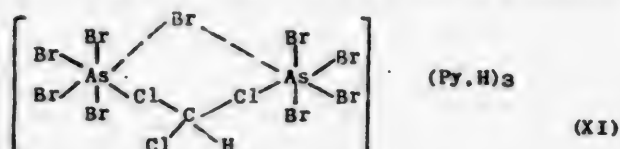


The following scheme is also possible:



but it is believed that it is much less probable: it is unlikely that two similar atoms would have different coordination numbers.

In 3:2:1 the CHCl_3 molecule may bring about a bond between the separate molecules of the complex. For simplicity the form 3:2:1 can be presented as:



Since no reliable data on the existence of complex crystals with the coordination number (5) [28] are available, it is desirable to take x-ray pictures of the compounds of the types 2:1:0 and 3:2:0 in order to determine the true coordination number of these complexes in the crystalline state.

Thus, it is possible to list the following basic structural schemes (Table 3).

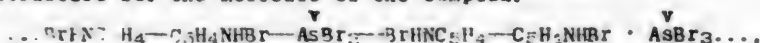
Type	Structure	Coordination number
1:1	$[\text{AsX}_4](\text{R.H})$	4
1:2	$[\text{X}_3\text{As} - \text{X} - \text{AsX}_3](\text{R.H})$	4
2:1	$[\text{AsX}_5](\text{R.H})_2$	5
3:2	$[\text{X}_4\text{As} - \text{X} - \text{AsX}_4](\text{R.H})_3$	5
3:1	$[\text{AsX}_6](\text{R.H})_3$	6
5:2	$[\text{X}_5\text{As} - \text{X} - \text{AsX}_5](\text{R.H})_5$	6

These schemes explain the ease of transformation between 2:1:0 and 2:1:1; they have no two- and three-membered bridges. Also in favor of coordination number 5 for 2:1:0 and 3:2:0 is the fact that only these forms gave solvated compounds in our experiments thus exhibiting a tendency towards the formation of complexes with a coordination number 6. Some results follow on the synthesis of complexes of hydrogen bromide $\gamma\gamma'$ -dipyridyl with AsBr_3 . Two complexes were obtained:

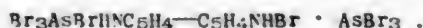


The first is formed in the presence of an excess of AsBr_3 , and the second in the presence of an excess of dipyridyl salt.

An unusual occurrence is that in the presence of an excess of AsBr_3 , a complex with a smaller content of arsenic bromide is formed; this can be interpreted by postulating a chain-like structure for the molecule of the complex:



whereas, for the second compound the following scheme would be likely:



An attempt will be made on the basis of the schemes to explain some of the characteristics of the compounds.

The decrease in the coordination number with the transition in the series Cl-Br-I and Bi-Sb-As may be understood without special explanations from a comparison of the effective radii of these ions, with due consideration of the increase of polarizability from Cl to I :

Bi 1.63 Å (?)	Cl 0.99
Sb 1.41	Br 1.14
As 1.21	I 1.33

An apparent anomaly is the absence of the quinoline derivatives for forms 5:2 and 3:2. This may be explained by assuming that three organic radicals in the complexes of these types are distributed about the central halogen atom. For quinoline such a distribution becomes difficult because of the large dimensions of its molecule.

As shown by the data in this investigation, the field of double halogenides of the elements of the arsenic sub group have been barely investigated; this is particularly so with respect to the derivatives of AsX_3 and SbX_3 . Interesting regularities might be expected here. This would be of importance for the theory of the structure of complex compounds, as well as supplementing existing data on the higher order organic compounds.

EXPERIMENTAL

Condensation with $\text{C}_9\text{H}_7\text{NHBr}$ with AsBr_3

1. To a hot solution of 4.78 g $\text{C}_9\text{H}_7\text{NHBr}$ (3.15 moles) in 50 ml. CHCl_3 was added over a period of 10 min. a solution of AsBr_3 in 40 ml CHCl_3 . A copious precipitate of yellow prisms separated. The crystals were washed with chloroform and dried in vacuo. The composition corresponds to the formula: $2\text{C}_9\text{H}_7\text{NHBr} \cdot \text{AsBr}_3$; m.p. 136-138°C.

0.1726 g. substance:	0.2194 g. AgBr.
0.1626 g. substance:	32.5 ml. 0.01376 N. I.
Found %:	As 10.31; Br 54.09
$2\text{C}_9\text{H}_7\text{NHBr} \cdot \text{AsBr}_3$. Calculated %	As 10.20; Br 54.39

On the recrystallization of this precipitate a slightly yellow precipitate of prismatic needles was separated from the mother liquor. Composition: $\text{C}_9\text{H}_7\text{NHBr} \cdot \text{AsBr}_3$; m.p. 148°C.

0.1858 g. substance:	0.2664 g. AgBr
0.1474 g. substance:	41.8 ml. 0.01376 N. I.
Found %:	As 14.62; Br 61.01
$\text{C}_9\text{H}_7\text{NHBr} \cdot \text{AsBr}_3$. Calculated %:	As 14.28; Br 60.93

The precipitate was recrystallized from chloroform without any change in composition.

Condensation of $\text{C}_9\text{H}_7\text{N} \cdot \text{C}_6\text{H}_5\text{Br}$ and $\text{C}_9\text{H}_7\text{N} \cdot \text{C}_4\text{H}_9\text{Br}$ with AsBr_3

2. To a solution of 5.25 g. (1.77 moles) AsBr_3 and 50 ml. CHCl_3 was added over a period of 50 minutes a solution of 2.24 g. $\text{C}_6\text{H}_5\text{Br}$ in 70 ml. CHCl_3 .

After adding approximately half of the solution of quinoline, a slightly yellow fine crystalline precipitate separated. The precipitate was filtered from the mother liquor, washed with chloroform (20 ml. x 2) and dried in vacuo.

The composition of the complex $\text{C}_6\text{H}_5\text{Br} \cdot 2\text{AsBr}_3$; m.p. 95-97°C.

0.0414 g. substance:	9.8 ml. 0.01925 N. I.
0.0500 g. substance:	11.95 ml. 0.01925 N. I.
0.0518 g. substance:	0.0782 g. AgBr.
Found %:	As 17.07; 17.23; Br 64.24.
$\text{C}_6\text{H}_5\text{Br} \cdot 2\text{AsBr}_3$. Calculated %	As 17.27; Br 64.50.

In the treatment of this precipitate with hot chloroform followed by cooling, heavy yellow crystals, bipyramidal hexahedral prisms, separated from solution. Composition $\text{C}_6\text{H}_5\text{Br} \cdot \text{AsBr}_3$, I., with an admixture of plate-like lighter crystals of yellowish color having the composition of the initial product (II). The separation of II from I was carried out by decantation:

I. 0.0572 g. substance:	10.7 ml. 0.01925 N. I.
0.0598 g. substance:	0.1332 g. AgBr
Found %:	As 13.49; Br 57.78.
$\text{C}_6\text{H}_5\text{Br} \cdot \text{AsBr}_3$. Calculated %:	As 13.55; Br 57.84
II. 0.0952 g. substance:	22.9 ml. 0.01925 N. I.
Found %:	As 17.34
$\text{C}_6\text{H}_5\text{Br} \cdot 2\text{AsBr}_3$. Calculated %:	As 17.27.

The residue from the multiple treatment with hot chloroform of complex $\text{ChC}_2\text{H}_5\text{Br} \cdot 2\text{AsBr}_3$ had a greenish yellow coloration and by analysis had a composition close to the formula: $2\text{ChC}_2\text{H}_5\text{Br} \cdot \text{AsBr}_3$, m.p. 180-182°C.

0.1548 g. substance:	20.9 ml. 0.01925 N. I
0.0886 g. substance:	12.00 ml. 0.01925 N. I
0.0460 g. substance:	0.0562 g. AgBr
Found %:	As 9.73, 9.76; Br 51.99
$2\text{ChC}_2\text{H}_5\text{Br} \cdot \text{AsBr}_3$. Calculated %:	As 9.48; Br 50.53

3. To a solution of 2.27 g. (1 mole) $\text{ChC}_2\text{H}_5\text{Br}$ in 100 moles CHCl_3 over a period of 23 minutes was added a solution of 3.0 g. AsBr_3 in 50 ml. CHCl_3 . After adding approximately a third of the solution of AsBr_3 a light greenish-yellow precipitate separated.

Upon completion of addition of the solutions, the precipitate was separated from the mother liquor, washed with chloroform and dried in vacuo. The analysis of precipitate gave low results for the product of composition $\text{ChC}_2\text{H}_5\text{Br} \cdot \text{AsBr}_3$, i.e.

11.54% As and 55.95% Br	
0.1212 g. substance:	19.4 ml. 0.01925 N. I
0.1188 g. substance:	0.1562 g. AgBr

On boiling the precipitate with chloroform, some was dissolved; by cooling the solution slowly, crystals of the complex $\text{ChC}_2\text{H}_5\text{Br} \cdot \text{AsBr}_3$, with a m.p. 130-132°C separated.

0.1000 g. substance:	18.5 ml. 0.01925 N. I
Found %:	As 13.34
$\text{ChC}_2\text{H}_5\text{Br} \cdot \text{AsBr}_3$. Calculated %:	As 13.55.

All the complexes of ethylquinoline bromide are hygroscopic; they decompose slowly in air, and are sparingly soluble in water.

4. To a solution of 2.22 g. of n butylquinoline bromide (1.0 mole) in 100 ml. CHCl_3 over a period of 30 minutes was added a solution of 2.67 g. AsBr_3 in 50 ml CHCl_3 . Upon completion of addition, a very thick yellow oil collected on the bottom of the reaction flask. After one day a considerable part of the oil crystallized. Needle-like, light yellow crystals were separated from the residual oil, washed with chloroform (20 ml. x 2) and dried in vacuo.

The composition corresponds to the formula $\text{ChC}_4\text{H}_9\text{Br} \cdot \text{AsBr}_3$; m.p. 78°C.

0.0362 g. substance:	6.4 ml. 0.01925 N. I
0.0594 g. substance:	10.2 ml. 0.01925 N. I
0.0770 g. substance:	0.0988 g. AgBr
Found %:	As 12.80, 12.47; Br 54.60
$\text{ChC}_4\text{H}_9\text{Br} \cdot \text{AsBr}_3$. Calculated %:	As 12.90; Br 55.05.

The crystals are hygroscopic and decompose slowly in the air. Recrystallization from chloroform (slightly soluble) gave no uniform product.

Condensation of α - and β - $\text{CH}_3\text{C}_5\text{H}_4\text{NHBr}$ with AsBr_3

5. To a solution of 11.18 g. (3.2 moles) AsBr_3 in 50 ml. CHCl_3 over a period of 30 minutes was added a solution of 1.94 g. α -picolinehydrobromide in 80 ml. CHCl_3 . A white crystalline precipitate separated. The precipitate after washing with chloroform (10 ml. x 2) and drying, according to the analytical data (As 16.4%, Br 63.7%) is not an individual substance.

After recrystallization from the mother liquor, the precipitate was changed to colorless plates of m.p. 63-65°C, with the composition according to analytical data, corresponding to the formula:

$\alpha\text{-CH}_3\text{C}_5\text{H}_4\text{NHBr} \cdot \text{AsBr}_3$	
0.1644 g. substance:	16.5 ml. 0.04019 N. I
0.2656 g. substance:	0.4076 g. AgBr
Found %:	As 15.11; Br 65.30
$\text{C}_6\text{H}_7\text{NHBr} \cdot \text{AsBr}_3$. Calculated %:	As 15.33; Br 65.41.

(In collaboration with R. Kulikova.)

Upon recrystallization from pure chloroform, this complex crystallized with an admixture of yellow rhombic plates, with an appearance similar to the crystals obtained in experiment 6, and having the composition $3C_6H_7NHBr \cdot 2AsBr_3$. The yellow crystals were obtained in a small amount, insufficient for purification and analysis. The main product has the composition $C_6H_7NHBr \cdot AsBr_3$, m.p. 63-65°C.

0.1746 g. substance: 18.5 ml. 0.04019 g. I
 0.1114 g. substance: 0.1712 g. AgBr
 Found %: As 15.95; Br 65.40
 $C_6H_7NHBr \cdot AsBr_3$. Calculated %: As 15.33; Br 65.41.

6. To a solution of 9.23 g. (3 moles) α $CH_3C_5H_4NHBr$ in 50 ml. $CHCl_3$, a solution of 5.58 g. $AsBr_3$ in 50 ml. $CHCl_3$ was added over a period of 8 minutes. A yellow, oily liquid separated which, after separation of the mother liquor and vacuum drying, crystallized. The crystals - yellow rhombic plates, after washing with chloroform (20 ml. x 2) melted at 97-100°C and had a composition corresponding to the formula:

$3\alpha \cdot CH_3C_5H_4NHBr \cdot 2AsBr_3$.
 0.1250 g. substance: 21.3 ml. 0.02057 g. I
 0.3880 g. substance: 0.5672 g. AgBr
 Found %: As 13.13; Br 62.21
 $3C_6H_7NHBr \cdot 2AsBr_3$. Calculated %: As 13.01; Br 62.47

Upon recrystallization from $CHCl_3$, this complex was transformed to $CH_3C_5H_4NHBr \cdot AsBr_3$; m.p. 63-65°C.

0.2490 g. substance: 28.6 ml. 0.03545 g. I
 0.2358 g. substance: 0.3592 g. AgBr.

7. To a solution of 17.99 g. $AsBr_3$ (2.0 moles) in 50 ml. $CHCl_3$, a solution of 4.97 g. β $CH_3C_5H_4NHBr$ in 50 ml. $CHCl_3$ was added over a period of 10 minutes. The yellow oil formed upon condensation was washed three times with chloroform (20 ml. x 3) and dried in vacuo. The oil crystallized into yellow crystals, having no definite composition (As 16.5%; Br 57.7%).

The precipitate was twice boiled with pure chloroform. When heated with $CHCl_3$ the crystals were changed to an oil, which upon cooling changed completely to slightly yellow rhombic plates of composition $\beta \cdot CH_3C_5H_4NHBr \cdot AsBr_3$; M.P. 61-63°C.

0.1486 g. substance: 34.30 ml. 0.01785 g. I
 0.2770 g. substance: 0.4288 g. AgBr
 Found %: As 15.43; Br 65.87
 $C_6H_7NHBr \cdot AsBr_3$. Calculated %: As 15.33; Br 65.41.

8. To a solution of 6.65 g. (3.9 moles) $\beta \cdot CH_3C_5H_4NHBr$ in 40 ml. $CHCl_3$ was added a solution of 3.04 g. $AsBr_3$ in 30 ml. $CHCl_3$ over a period of 30 minutes. A yellow oil was separated which started to crystallize after 5 hours (temp. 16°C). After a day the oil was completely changed to a mass of crystals - slightly yellow rhombic plates. The crystals were washed with chloroform and dried in vacuo. Composition $2\beta \cdot CH_3C_5H_4NHBr \cdot AsBr_3$. m.p. 136°C.

0.1806 g. substance: 20.5 ml. 0.02695 g. I
 0.2796 g. substance: 0.3962 g. AgBr
 Found %: As 11.46; Br 60.30
 $2C_6H_7NHBr \cdot AsBr_3$. Calculated %: As 11.31; Br 60.30

Attempts to recrystallize this complex failed because of its very slight solubility in chloroform.

Condensation of $C_6H_5NC_2H_5Br$ and $C_6H_5N \cdot C_4H_9Br$ with $AsBr_3$.

9. To a solution of 5.0 g. (1.04 ml) $C_6H_5NC_2H_5Br$ in 100 ml. $CHCl_3$ was added a solution of 8.0 g. $AsBr_3$ in 50 ml. $CHCl_3$ over a period of 20 min. The light yellow precipitate was washed with chloroform and dried in vacuo. According to analytical data, this product is not an individual substance (As 13.6%; Br 65.7%). Recrystallization of this precipitate from chloroform yielded colorless plates of composition $C_6H_5NC_2H_5Br \cdot AsBr_3$, of m.p. 110-112°C.

* In collaboration with N. Pavlova.

0.1840 g. substance: 0.2760 g. AgBr
 0.3942 g. substance: 86.5 ml. 0.01797 N.I
 Found %: As 14.77; Br 63.83
 $C_5H_5NC_2H_5Br \cdot AsBr_3$. Calculated %: As 14.90; Br 63.58.

10. To a solution of 6.0 g. (2.00 moles) $C_5H_5NC_2H_5Br$ in 150 ml. $CHCl_3$ was added a solution of 5.0 g. $AsBr_3$ in 30 ml. $CHCl_3$ over a period of 15 minutes. A copious yellow precipitate separated. After washing with chloroform and drying in vacuo its composition corresponded to the formula: $2C_5H_5N \cdot C_2H_5Br \cdot AsBr_3$.

0.3156 g. substance: 0.4316 g. AgBr.
 0.2914 g. substance: 47.2 ml. 0.01797 N.I
 Found %: As 10.90; Br 58.19
 $2C_5H_5NC_2H_5Br \cdot AsBr_3$. Calculated %: As 11.00; Br 57.84.

Recrystallization of this precipitate from hot chloroform yielded light yellow needles, having the composition of the starting product:

0.254 g. substance: 0.3442 g. AgBr
 0.311 g. substance: 49.9 ml. 0.01797 I
 Found %: As 10.76; Br 57.57.

11. To a hot solution of 8.25 g. (5.1 moles) $n C_4H_9Br \cdot C_5H_5N$ in 70 ml $CHCl_3$ was added a solution of 2.36 g. $AsBr_3$ in 60 ml. $CHCl_3$ over a period of 7 minutes. The cloudy, yellow solution formed was heated to boiling. A yellow mobile oil settled on the bottom of the flask. After cooling, the mother liquor was decanted, and the oil was washed with chloroform (20 ml. x 2).

After washing, the oil crystallized in needle-like crystals of light yellow color. Composition $3C_5H_5N \cdot C_4H_9Br \cdot 2AsBr_3 \cdot CHCl_3$; m.p. 68-70°C.

0.1860 g. substance: 18.15 ml. 0.02875 N.I
 0.2010 g. substance: 0.2414 g. AgBr.
 Found %: As 10.51; Br 51.11.
 $3C_5H_5NC_4H_9Br \cdot 2AsBr_3 \cdot CHCl_3$. Calculated %: As 10.73; Br 51.49.

CONCLUSIONS

1. A new group of double halogenides of arsenic has been described.
2. The dependency between the composition of the given complexes and the nature of the initial components has been established.
3. A possible structural scheme for these complexes has been proposed.

LITERATURE CITED

- [1] J. A. Hayes, J. Am. Soc., 24, 360 (1902); Zbl., C, 1 1165 (1902). [2] A. Gutbier, 2. Muller, Z. allg. anorg. Ch., 128, 137 (1923). [3] Edinger, German patent No. 86148; Fndl., 4, 1139. [4] P. Popov, Journal of Gen. Chem.,

SYNTHESIS OF OLEFINIC AND PARAFFINIC HYDROCARBONS

VI. DIOLEFINIC HYDROCARBONS IN THE SYNTHESIS OF HYDROCARBONS WITH CENTRALLY LOCATED DOUBLE BOND

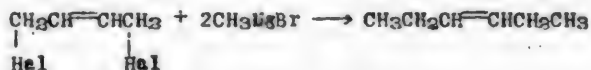
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The reaction between allyl bromide or chloride and magnesium organic compounds [1,2] represents a general method for the synthesis of 1-alkenes. Many studies have been made of the reaction of allyl bromide as chloride homologs with various magnesium organic compounds. These investigations have shown that the presence of a double bond promotes the mobility of the halogen atom. This occurs in all instances, independent of the location of the halogen atom with respect to the primary carbon atom: (thus, for a primary compound, butadienehydrochloride [3], isopropenehydrochloride [4,5] and hydrobroside [6]); secondary: secondary butadienehydrochloride [3], diisocrotylhydrochloride [3], piperylene hydrochloride [3]; or tertiary: in hydrobromide of 2,4-dimethylpentadiene-1,3 [6,7] by carbon atoms. Thus the mobile halogen atom can be readily replaced by a radical in the presence of magnesium organic compounds. These reactions are therefore of use as a general method for the synthesis of alkenes of varying structures.

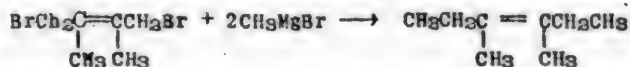
1,4-Dichlorobutene-2 is the simplest type of unsaturated dihalogenide derived from an allyl compound. Each halogen atom, being under the activating influence of the same double bond should be mobile and capable of being readily replaced by a radical group in the presence of magnesium organic compounds. This reaction could be used as a method for the synthesis of alkenes with a centrally located double bond.

This paper deals with an investigation of the reaction between 1,4-dihalogenides of divinyl (1,4-dichloro-2-butene and 1,4-dibromo-2-butene) with methyl-magnesium bromide. It has been established for the first time that in this reaction both halogen atoms are replaced by a methyl group with the formation of hexene-3, an alkene with a centrally located double bond.



The initial material, alkadiene-butadiene-1,3, was recovered as a side product in the reaction, the splitting off of halogen from the dihalogenide.

Two unsuccessful attempts to carry out similar reactions have been reported in the literature. In 1922 Braun and Leuke [8] obtained a high boiling resin in the reaction between phenylmagnesium bromide and 1,4-dibromo-2-butene. Its composition has not been investigated in detail. In 1928 Macallum and Whitby [9] studied the reaction of 1,4-dibromo-2,3-dimethylbutene-2 with methylmagnesium iodide and established that, instead of the formation of the more likely 3,4-dimethyl-3-hexene,



the reaction product was the initial 2,3-dimethylbutadiene-1,3 together with its two oily dimers.

EXPERIMENTAL

Bromination of butadiene 1,3 was conducted at 20-25°C in a chloroform solution with constant stirring. The solid obtained, 1,4-dibromo-2-butene, recrystallized from petroleum ether, had a m.p. of 52-53°C.

Literature data by Thiele [10], Braun and Lenke [8], Farmer, Lawrence and Thorpe [11]: m.p. 52-53°C.

Liquid 1,2-dibromo-3-butene, obtained together with solid dibromide in the bromination of butadiene 1,3 was converted by heating [11] to solid dibromide, identical with 1,4-dibromo-2-butene; the latter is obtained directly in the bromination of butadiene. Yield of 1,4-dibromo-2-butene 60% of theoretical.

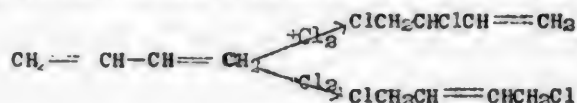
Chlorination of butadiene 1,3 (technical) was carried out using different solvents and temperatures. The reaction products were fractionated twice (tall Vigreux column). The experimental results are listed in Table 1.

TABLE 1

Experiment No.	Butadiene-1,3	Solvent	Temperature of experiment	Yield of dichlorides (% of theoretical)	Weight ratio of 1,2-dichloride to 1,4-dichloride
1	Gas	---	10-15°C	---	2:1
2*	Gas	Chloroform	-18	---	2.9:1
3	Liquid	Chloroform	-18	42	2.5:1
4	Liquid	Ether	-20	41	2.3:1
5	Liquid	---	Cooling with dry ice	53	1.5:1

Together with the dichloride, an appreciable amount of high boiling fractions, containing apparently, butadiene tetrachloride, were obtained in each experiment. (In some experiments yields up to 60% were obtained, based on butadiene taken for the reaction).

As shown in table 1, independent of the experimental conditions, the fraction of a b.p. 115-117°C (see Table 2), containing 1,2-dichloro-3-butene (1,2-divinyldichloride), is obtained in larger amounts than 1,4-dichloro-2-butene (1,4-divinyldichloride):



The experimental values of the dichlorides and those from the literature, including the data for 2,3-dichlorobutane are given in Table 2.

Myskat and Northrup [12] established in the investigation of ozonization products of butadiene 1,3 that the low boiling dichloride is 1,2-dichloro-3-butene and the high boiling 1,4-dichloro-2-butene. Differing from the dibromides, the butadiene dichlorides, when heated do not undergo allyl rearrangement.

1. Interaction of 1,4-dibromo-2-butene with methylmagnesium iodide.

To methylmagnesium iodide (188 g. methyl iodide and 32 g. magnesium), filtered off in the presence of nitrogen from the residual unreacted magnesium, was added slowly with constant stirring an ether solution of freshly crystallized (from petroleum ether) 1,4-divinyldibromide (60 g.). The reaction mixture was then heated on a water bath for 10 hours. The decomposition was accomplished by dilute acetic acid (10%). After distilling off the ether from the washed and dried ether extract a crystalline substance separated in the distilling flask. After removing the crystals, the liquor was separated by fractional distil-

l. The second series of experiments was carried out by the method described by Myskat and Northrup [12].

lation, 2.5 g. of 3-hexene (b.p. 66.5-67.5°C (755 mm.); see section 4). This represented a yield of 10-12% of theoretical. The crystals (2 g.) after recrystallization from petroleum ether, melted at 117°C; this corresponds to the literature data for one of the butadiene tetrabromides [9]. The melting point of a mixed sample of the substance with crystalline butadiene tetrabromide gave no depression. Thus, a reaction of disproportionation of bromide between two molecules of 1,4-dibromo-2-butene has taken place:



The reaction between 1,4-dibromo-2-butene and methylmagnesium iodide was also conducted under other conditions -- by cooling with ice during the process of adding the dibromide, exposing the reaction mixture to ultra violet light, and also adding the reagent in reverse order. The yield of hexene-3 in all these experiments was about the same.

Table 2

Dichloride	Boiling point	n_D	d_4^{20}	M_R		References
				Found	Calculated	
1,2-Dichlorobutene-3	115 - 117°C (750 mm)	1.4475 (20°C)	1.1170	29.74	29.94	Obtained in the present investigations.
	45 - 45.5 (40 mm)	1.4550 (30.5°C)				[12]
	115 (750 mm)					[12]
	38 - 45 (40 mm)					[21]
	41 - 41.5 (40 mm)	1.4641				[22]
2,3 Dichlorobutane	115 - 118°C	1.4435 (18°)	1.1070			[12]
1,4-Dichlorobutene-2	158°C (750 mm)	1.4885 (20°)	1.1830	30.50	29.94	Obtained in the present investigations.
	75 - 78 (40 mm)	1.4745				[12]
	145 (760 mm)	(30.5°)				[12]
	74.5-75.5 (40mm)	1.4890 (20°)	1.1825	30.50		[21]
	75 - 76 (40 mm)	1.4892 (20°)				[22]

2. Interaction of 1,4-dichloro-2-butene (1,4-divinyl dichloride) with methylmagnesium bromide

To methylmagnesium bromide (75 g. methylbromide and 16 g. magnesium), filtered off in a nitrogen atmosphere from the residual undissolved magnesium, was added with constant stirring, an ether solution of 1,4-dichloro-2-butene (37 g.). After addition of the dichloride, the reaction mixture was allowed to stand overnight; on the following day the stirring was continued for eight hours at room temperature, followed by four hours of heating on a water bath. The decomposition was carried out by dilute acetic acid (10%). After distilling off the ether from the neutral reaction product and drying the latter with calcium chloride

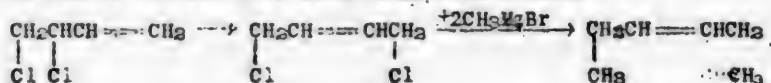
*) The fraction of b.p. 115-117°, judging by its constants, contained a considerable amount of dichlorobutane formed from pseudobutylene (present in technical divinyl). Since the yield of this fraction, based on the initial technical divinyl, attained 30% (See experiment 3, Table 1) and the content of pseudobutylene in technical divinyl attains 12%, the fraction of b.p. 115 - 117° contained about 40% dichlorobutane.

the ether extract was fractionated. The product was 6 g. of 3-hexene, b.p. 66.5 - 67.5°C (754 mm) (see section 4); i.e., a yield of 24% of theoretical. The adsorption of the gas liberated in the reaction by bromine showed that about 50% of the dichloride taken for the reaction was converted to divinyl - 60 g. of divinyltetrabromide, m.p. 117°C, was formed (after recrystallization from petroleum ether).

The reaction between 1,4-dichloro-2-butene and methylmagnesium bromide was also conducted under other conditions -- cooling with ice while adding dichloride, stirring the reaction mixture for 12 hours at room temperature only, and adding the reagents in reverse order. The yield of 3-hexene in all these experiments was lower (15 - 20% of theoretical), than that obtained in the first mentioned experiment.

3. Reaction of 1,2-dichloro 3 butene (1,2-divinyl dichloride) with methylmagnesium bromide

The reaction of 1,2-dichloro 3 butene (41 g.) fraction of a b.p. 115-117°C with methylmagnesium bromide (75 g. methyl bromide and 16 g. magnesium) was conducted under conditions similar to those described in section 2. Fractional distillation of the reaction product yielded 4.5 g. of 3 hexene, b.p. 66.5 - 67.6°C (755 mm) (see section 4). Thus, 1,2-dichloro 3 butene undergoes an allyl rearrangement during reaction forming 1,4-dichloro-2-butene which reacts further with methylmagnesium bromide:



It should be pointed out that in the distillation of the reaction product a fraction of b.p. 115 - 117°C (18 g., i.e. 45% based on the dichloride taken for the reaction) was collected: this corresponded to 2,3 dichlorobutane; b.p. 115-117°C, n_D^{20} 1.4430, d_4^{20} 1.1090. (The literature data for dichlorobutane are given in Table 2).

Thus, the yield of hexene-3, based on reacting 1,2-dichloro-3-butene, attains 40% of theoretical. The separation of divinyl, identified as a crystalline tetrabromide, was also observed in this reaction.

4. Purification and identification of 3-hexene

3 Hexene obtained in different experiments was treated with a solution of metallic sodium in liquid ammonia in order to remove any traces of halogen present [4]. 3-Hexene purified by distilling over sodium (on a column with 25 theoretical plates) had the following constants:

b.p. 66.9 - 67.4°C (758 mm); n_D^{20} 1.3938; d_4^{20} 0.6761; MW_D 29.76.

C_6H_{12} Calculated: MW_D 29.44

In Table 3 are given the literature data for cis- and trans hexene.

Table 3				
Hexene	Boiling point	n_D^{20}	d_4^{20}	References
	66.6 - 67°C	1.3942	0.6816	[13]
	64°C	1.3940 (at 19°)	0.6807 (at 19°)	[14]
Cis	66.8 - 66.9° (751 mm)	1.39338	0.67967	[15]
Trans-	67.4 - 67.6 (741 mm)	1.3937	0.67782	[15]
Cis-	66.85 - 67.15	1.3930	0.6780	[16]
Trans-	66.4 - 66.7	1.3943	0.6794	[16]

4.355 ml substance: 13.649 mg. CO₂; 5.616 mg. H₂O.
 2.973 ml substance: 9.310 mg. CO₂; 3.826 mg. H₂O.
 Found % C 85.48, 85.41; H 14.33, 14.30.
 C₆H₁₂. Calculated %: C 85.52; H 14.48

3-Hexene was oxidized by using a 2% aqueous solution of potassium permanganate. The oxidation product was propionic acid, b.p. 138.5 - 142°C; its anilide had a m.p. of 103 - 103.5°C, corresponding to the literature data (Crossley and Perkin [17], m.p. 103 - 101°C).

The bromination of 3-hexene was conducted in an ether solution while cooling the reaction with ice. From 5 g. of 3-hexene, 12 g. (yield 86% of theoretical) of 3,4-dibromohexane, having the following constants was obtained:

b.p. 64.5 - 65°C (6 mm).
 n_D^{20} 1.5090, d_4^{20} 1.6105, M_R 45.29.
 C₆H₁₂Br₂. Calculated: M_R 45.44.

Literature data: Risseghem [18] b.p. 82.5 (16 mm.); Schmitt and Boord [13]: l.b.p. 80 - 81 (13 mm), n_D^{20} 1.5045, d_4^{20} 1.6027; Lespieau and Wiemann [14] 73 - 74°, (10 mm), n_D^{20} 1.5042, d_4^{20} 1.5995.

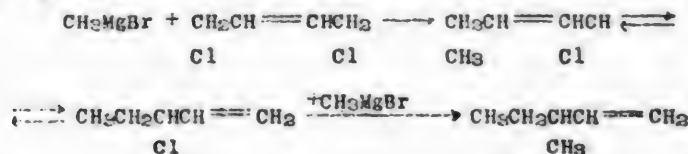
5. Optical investigation of 3-hexene

A Raman spectrum of 3-hexene was taken on a glass triprismatic Steinchel spectrograph with an average linear dispersion in the region of 4358-4916 Å of 0.08 mm/Å. The illuminator had three mercury lamps IGAR-2. The excitation was conducted by the line of 4358 Å. A solution of potassium nitrite was used as a light filter. The measurements of the frequencies were made by using a standard spectrum of an iron arc, using Hartman's diaphragm. The accuracy of frequency measurements was 2.4 cm⁻¹. The intensity of the spectrum lines was evaluated visually. The Raman spectrum for 3-hexene was investigated in the interval of frequencies from 0 to 2000 cm. The results of measurements of the frequencies of Raman spectrum for 3-hexene are:

221 (0.4), 406 (2;B), 470 (2), 567 (1.2), 718 (0.2), 746 (0.2), 769 (0.8),
 824 (2.8; B; b), 839 (2.4), 875 (1.6), 897 (2.8), 1002 (6), 1040 (1.2), 1068 (6),
 1107 (0.2), 1165 (0.8), 1202 (1.2), 1258 (8;B), 1296 (0.4), 1304 (10), 1353 (0.2),
 1376 (1.2), 1442 - 1460 (10; B), 1660 (4), 1672 (40).

The absence of frequency 1642 cm⁻¹ indicates that the preparation under investigation had no traces of any α-olefin [20].

The formation of α-olefin hydrocarbon in the interaction of 1,4-divinyl dichloride with methyl magnesium bromide could have taken place according to the following reaction:



From literature data [19, 20] it is known that for a double carbon-carbon bond, located between two ordinary bonds the following two frequencies are characteristic: 1658 and 1673 cm⁻¹, belonging to cis- and trans-isomers, respectively. The presence of the line 1672 cm⁻¹ in the spectrum of 3-hexene so indicates that an almost pure trans-form is present. The weak line 1660 cm⁻¹ indicates the presence of a small amount of cis-form; its concentration is approximately 9% (not greater), assuming that the intensity of the characteristic frequency of the bond C=C for cis- and trans- forms is approximately the same.

* For the characteristics of the combination lines the following designations are introduced:
 B - wide band b - background the line in the position of the background of high intensity.

CONCLUSIONS

1. It has been shown for the first time that 1,4 divinyl dihalogenides can react with organic magnesium compounds forming alkenes with a centrally located double bond.
2. It has been established that 1,2-divinyl dichloride in the interaction with magnesium organic compounds undergoes allyl rearrangement to 1,4 divinyl dichloride; this forms an alkene with a centrally located double bond.
3. The reaction of methylmagnesium iodide with 1,4-divinyl dibromide yields 3 hexene (yield 10% of theoretical). The reaction of methyl magnesium bromide with 1,4-divinyl dichloride and with 1,2 divinyl dichloride yields 3 hexene (yields of 24 and 40% respectively).
4. 3-Hexene was identified by its physical properties, by investigation of its oxidation products, by bromination and by examination of its Raman spectrum.

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ELECTROLYTIC HYDROGENATION OF DIMETHYLACETYLENYLCARBINOL

II. Effect of the Cathode Surface and Concentration of Dimethylacetylenyl Carbinol in the Electrolyte

A. I. Lebedeva

The results of an investigation of the electrolytic hydrogenation of dimethylacetylenylcarbinol and dimethylvinylcarbinol using cathodes made from various metals were reported previously [1]. As noted therein, the preliminary treatment of the metal surface greatly influenced the hydrogenation process.

Tafel [2], during his first experiments on electrolytic hydrogenation of caffeine, noted that the course of the reaction depends mainly on two factors: 1) mechanical properties of the lead surface and 2) the presence of foreign salts in the electrolyte. A completely smooth lead cathode was unsuitable for the electro-reduction of caffeine in a sulfate solution. A "prepared" lead cathode gave good results. The specific effect of the cathode surface was particularly noticeable in the hydrogenation of unsaturated acids [3]. No hydrogenation takes place on platinum cathodes; with platinized platinum, stearic acid is obtained in good yields.

Previous experiments on electrolytic hydrogenation on smooth platinum, platinized platinum, and nickel black showed that the surface of the cathode had a great influence on the process of electrolytic hydrogenation. On cathodes made from the same material the hydrogenation proceeded with a different rate depending on previous treatment of the cathode surface.

It was therefore decided for the present investigation to study in detail the effect of the surface of the copper and silver cathodes on the rate of electrolytic hydrogenation of dimethylacetylenylcarbinol to dimethylvinylcarbinol.

The following surfaces, treated differently, have been tested: 1) smooth red copper; 2) copper, coated by displacement on iron (contact copper on iron); 3) red copper - cleaned with emery; 4) copper with a layer of electrolytic copper from an ordinary copper bath; 5) spongy copper, coated electrolytically on red copper; 6) silver, coated on copper by displacement from a dilute silver nitrate solution (contact silver on copper).

In Table 1 are listed the results of the experiments:

For hydrogenation 20 g. of dimethylacetylenylcarbinol was taken in each experiment. The hydrogenation was continued in all experiments until a test for acetylenic hydrogen was negative (test with ammoniacal solution of silver oxide). As Table 1 indicates, the highest rate of hydrogenation was observed on cathodes made from spongy copper. However, the yield of dimethylvinylcarbinol in this experiment was quite low. For a comparison of the results of hydrogenation, the last column of Table 1 indicates the time required to obtain, under given conditions, 10 g. of dimethylvinylcarbinol. This column indicates that on a copper surface, coated on iron by a displacement method, hydrogenation takes place approximately six times slower and on smooth copper five times slower than of a silver surface coated by the displacement method on copper. On a copper surface, treated with dilute silver nitrate, 3.3 hours are required for obtaining

under given conditions 10 g. of dimethylvinylcarbinol. Silver or silver coated cathodes are distinguished by the fact that they are less sensitive to contaminations than copper cathodes. The latter required a new treatment after each experiment. With copper cathodes coated with contact silver, several experiments in succession could be conducted without any treatment. In Table 2 are given the data on the experiments on repeated hydrogenation on the same contact silver surface.

TABLE 1

No. of Experiment	Material and surface of cathode	Duration of hydrogenation in hours	Yield of dimethylvinylcarbinol		Time required to obtain 10g dimethylvinylcarbinol, hrs.
			g.	%	
1	Smooth red copper	16.7	10.4	50.0	16.0
2	Contact copper on iron	16.2	7.8	38.2	20.8
3	Copper, cleaned with emery	12.4	10.6	51.8	11.7
4	Electrolytic copper on red copper	8.4	15.6	76.20	5.4
5	Spongy copper on red copper	4.7	11.4	55.6	4.1
6	Contact silver on copper	5.9	17.9	87.4	3.3

TABLE 2

No. of Experiment	Duration of hydrogenation in hours	Yield of dimethylvinylcarbinol		Time required to obtain 10 g. dimethylvinylcarbinol, hours
		g.	%	
1	6.1	16.9	78.0	3.8
2	6.5	15.4	75.5	4.2
3	6.6	15.4	75.5	4.3

As Table 2 reveals, the time of hydrogenation is increased for each subsequent experiment only slightly: the yield of dimethylvinylcarbinol is almost the same. The same stability of the silver coated copper surface was observed in a number of other experiments.

In Table 3 are given the data on electrolytic hydrogenation on a copper cathode, first coated with a layer of copper oxide by igniting on a burner. The experiments differed from the previous ones also in that the hydrogenation was carried out without separating the cathode and anode space with a diaphragm.

For this experiment 10 g. of dimethylacetylenylcarbinol was taken. As Table 3 reveals the rate of hydrogenation in this experiment approached the rate of hydrogenation on the copper cathode cleaned with emery. A detailed comparison could not be made because of the variable experimental conditions.

The data given in Table 3 indicate the variation in the content of dimethylacetylenylcarbinol and dimethylvinylcarbinol in the electrolyte during the hydrogenation process. The maximum content of dimethylvinylcarbinol in the electrolyte did not occur at the end of hydrogenation, but while 1.2% of dimethylacetylenylcarbinol still remained unhydrogenated. At the end of the hydrogenation the rate was lower and a loss of dimethylvinylcarbinol occurred. Probably some was carried out with the increasing current of hydrogen.

In order to determine clearly the rate of hydrogenation as a function of dimethylacetylenylcarbinol, experiments were conducted which are summarized in Table 4.

Under given experimental conditions, the optimum concentration is 150 g. of dimethylacetylenylcarbinol in 1000 ml. electrolyte. With a further increase in concentration of dimethylacetylenylcarbinol a rapid separation into layers of catholyte takes place: as a

TABLE 3

Duration of hydrogenation, hours	Amount of residual dimethylacetylenylcarbinol, g.	Yield of dimethylvinylcarbinol		Time required to obtain 10 g. dimethylvinylcarbinol, hours
		g.	%	
2	5.82	2.65	--	7.5
4	2.81	6.28	--	6.4
6	0.55	7.33	--	8.2
8	0.0	6.20	65	12.9

TABLE 4

Experiment No.	Amount of dimethylacetylenylcarbinol, taken for experiment, g.	Initial concentration of dimethylacetylenylcarbinol l/g	Duration of hydrogenation, hours	Yield of dimethylvinylcarbinol,		Time required to obtain 10 g. dimethylvinylcarbinol, hours
				g.	%	
1	20	50	6.20	16.1	78.7	3.10
2	40	100	8.35	29.5	72.0	2.08
3	60	150	7.80	44.7	73.0	1.30
4	80	200	19.6	57.0	69.5	2.45

result of this the rate of hydrogenation is decreased. An increase in concentration under given conditions is only possible by applying mechanical stirring.

EXPERIMENTAL

1. Effect of the cathode surface treated by different methods

The investigation of the effect of the cathode surface was carried out in an ordinary electrolyzer. The outer cylinder of the electrolyzer was made of copper; thus, the inner wall of the electrolyzer was also employed as a cathode. Outside, in the upper part of the electrolyzer, a terminal for the electric current was soldered. The copper electrolyzer was 280 mm. in height, and 100 in diameter.

In the center of the copper electrolyzer was placed a ceramic porous cylinder. The dimensions of the porous cylinder were: height 300 mm., inner diameter 73 mm., wall thickness. 8.5 mm.

A nickel wire used as an anode was packed along the inner wall of the porous cylinder. Diameter of nickel wire: 2 mm.

For temperature control of the cathode space, the electrolyzer was placed in a water bath with circulating tap water. The catholyte was poured into the space between the copper and ceramic cylinder to a height of 250 mm.; the working surface of the cathode was 7.85 dm².

The working surface of the anode: 5.5 dm². Catholyte: 20 g. of dimethylacetylenylcarbinol in 400 ml. aqueous sodium hydroxide (1 g. NaOH in 1000 ml. H₂O). Anolyte: 1000 ml. of saturated aqueous sodium hydroxide. Strength of current at the beginning of the experiment: 6 A, current density $6/7.85 = 0.77$ A/dm². At the end of the experiment the current strength dropped to 3 A. Voltage at the start of the experiment: 15 V, then dropped to 3.5-4.5 V. Temperature of catholyte: 20-25°C.

In the experiments of hydrogenation of the copper surface, the copper cylinder was first washed with dilute nitric acid, then with water. In all the other experiments the cylinder was washed with dilute nitric acid, water, and then subjected to the corresponding

treatment. In the precipitation of copper on iron, the iron cylinder had the same dimensions as the copper one. After ordinary cleaning, a solution of copper sulfate (10 g./l) was poured into the cylinder; after 10-15 minutes the solution was decanted, the cylinder washed and filled with the catholyte. The copper was precipitated on iron in a thin layer; during electrolysis this came off the iron, with the formation of some corrosive spots. The electrolytic copper was deposited on the copper cylinder from a bath as recommended by Blum and Hagaboom [4]. The electrodeposition of spongy copper was carried out by the method described by Borak, Bai shin and Gavrilov [5]. The formula recommended by them was used almost without any modification.

At a current density of about 11 A/ dm², 15 minutes after the current was started a sponge of about 10 mm. length was formed on the cathode. The length of this sponge has been found to increase with an increase in density; a long sponge, however, falls off more easily from the cathode surface. Upon completion of deposition, the treated copper sulfate was decanted, the electrolyzer washed with distilled water and filled at once with the catholyte. The washing was carried out very carefully, the liquid being decanted by means of a syphon, since the sponge came off easily from the surface of the cathode.

For the deposition of silver on the copper surface (contact silver on copper) the copper cylinder was first treated as described above. The silver nitrate solution was prepared as follows 2.5 3 g. of silver nitrate and 1 ml. of nitric acid (sp. gr. 1.4) were used per liter of water; 2200 ml. of this solution was introduced into the cylinder. After 10 15 minutes the inner surface of the copper cylinder was coated by an even velvet-like light gray deposit, the solution was decanted, the cylinder washed with water and at once filled with the electrolyte. Since the silver surface was multicolored and irregular, the surface of the cylinder was washed with dilute nitric acid and subjected to repeated treatment with a silver nitrate solution. With an increase in silver nitrate concentration, the time of contact could be reduced to 5 minutes. The silver layer was fairly stable. After washing with water the hydrogenation could be carried out repeatedly without retreating the cylinder (Table 2).

2. Investigation of the effect of concentration of dimethylacetylenylcarbinol in catholyte.

The experiments listed in Table 4 were carried out on contact silver, deposited on copper as described above, and in the same electrolyzer. For 400 ml. of catholyte, 20 g. of dimethylacetylenylcarbinol was taken in the first experiment, 40 g. in the second, 60 g. in the third, and in the fourth 80 g. In the last experiment the carbinol dissolved slowly and after 2 3 hours of hydrogenation a layer appeared on the surface characteristic of the completion of hydrogenation.

3. Testing of the copper surface, coated with copper oxide (Hydrogenation without a diaphragm)

The arrangement for the electrolytic hydrogenation of dimethylacetylenylcarbinol, with the cathode and anode space separated by a porous diaphragm, was very simple. The electrolyzer was an ordinary battery, on the inner wall of which was spread a perforated copper sheet used as a cathode. Before the start of the experiment the cathode was washed with dilute nitric acid (1:1), cleaned with emery and ignited, using a gas burner. The area of the cathode: 1.7 dm². Sheet nickel, rolled on a cylindrical glass rod, was used as an anode; this was placed in the center of the electrolyzer. The area of the anode: 1.5 dm². The distance between the cathode and anode: 5 mm. When the distance is increased the concentration of the alkali in the electrolyte should be increased. 10 g. dimethyl acetylenylcarbinol in 100 ml. aqueous sodium hydroxide (50 g. in 1000 ml.) was the electrolyte. Strength of current 1.4 A, voltage 2.8 - 2 V. Temperature of experiment: 20 25°C.

Upon completion of each experiment the product was saturated with carbon dioxide until acid to phenolphthalein (sodium hydroxide is converted to sodium bicarbonate). The mixture of dimethylacetylenylcarbinol and dimethylvinylcarbinol was distilled off. In the distillation of carbinol, without saturation with carbon dioxide, a noticeable decomposition of the acetylene alcohol and an increase in the acetone content in the mixture occurred; therefore experiments were conducted to find the best conditions for distilling off dimethylacetylenylcarbinol from the alkaline electrolyte. For each experiment 20 g. dimethylacetylenylcarbinol in 200 ml. aqueous sodium hydroxide (50 g. in 1000 ml.) was taken. In the first experiment 50 ml. was distilled off directly from the alkaline solution. This was then salted out with potassium carbonate and the upper layer weighed and analyzed. In the second experiment the alkaline layer was acidified with acetic acid until weakly acidic, and then distilled and treated as in the first experiment. In the third experiment the alkaline solution was saturated with carbon dioxide until acid to phenolphthalein; the subsequent treatment was the same as in the previous experiments. The results are summarized in Table 5.

TABLE 5

Experiment No.	Composition of electrolyte	Weight of upper layer, g.	Weight of pure dimethylacetylenylcarbinol, g.	Weight of acetone, g.	Loss of carbinol in distillation g.
1	Alkaline	20	17.6	1.58	2.4
2	Acidified with acetic acid	20.5	18.8	0.33	1.2
3	Saturated with carbon dioxide	20.3	19.2	0.25	0.8

Best results were obtained by saturating the alkaline electrolyte with carbon dioxide. The amount of acetone and the losses were less than occurred in the other experiments. A quantitative determination of dimethylacetylenylcarbinol was made by titrating an aqueous solution of sodium hydroxide in the presence of a large excess of silver nitrate by the method developed by Kh. I. Kondrat'ev. Acetone was quantitatively determined by use of a sodium hydroxide solution in the presence of hydroxylamine hydrochloride. The quantitative determination of dimethylvinylcarbinol was conducted by titrating a bromide-bromate solution in an acid medium. In saturating the electrolyte containing dimethylacetylenylcarbinol with carbon dioxide, a yellow precipitate of a copper derivative of dimethylacetylenylcarbinol was usually formed.

CONCLUSIONS

1. The rate of electrolytic hydrogenation of dimethylacetylenylcarbinol on a copper and silver cathode depends on the initial treatment of the cathode.
2. The rate of electrolytic hydrogenation of dimethylacetylenylcarbinol is greatest for a spongy copper surface; the rate of formation of dimethylvinylcarbinol is best for a silver surface coated on copper by the displacement method.
3. In the hydrogenation without stirring in a weak alkaline electrolyte the optimum concentration of dimethylacetylenylcarbinol in electrolyte was 150 g. per liter of electrolyte.
4. In the hydrogenation without a porous diaphragm the rate of electrolytic hydrogenation was essentially unchanged.

LITERATURE CITED

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April 16, 1947

ALLYL REARRANGEMENTS

X. ACTION OF ALCOHOLIC SOLUTIONS OF ALKALIES ON ISOMERIC BUTOXYCHLOROPENTENES

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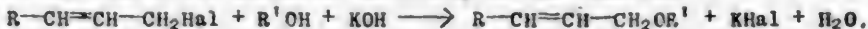
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The action of alcoholic solutions of alkalies and alcoholates of alkaline metals on primarily allyl halide isomers has been investigated by several research workers.

Claissen [1], by the reaction between potassium ethylate and phenolate on 1-bromo-3-methylbutene-2 obtained 1-ethoxy-3-methylbutene-2 and the phenyl ether of 3-methylbutene-2-ol-1, respectively. Prevost [2] by the reaction between potassium hydroxide in ethyl alcohol and crotylbromide obtained the ethyl ether of crotyl alcohol. Similar results were obtained by Meisenheimer and Link [3] and Tamele, Ott, *et al.* [4] in the reaction between cinnamylbromide and methallylchloride. By the action of potassium hydroxide in methyl, ethyl and isopropyl alcohols on methallylchloride, good yields of the corresponding ethers of methallyl alcohol were obtained.

Roberts, Young and Winstein [5] in the reaction between sodium alcoholate and crotyl chloride in absolute alcohol obtained the ethyl ether of crotyl alcohol; Young and Andrews [6] carried out this reaction in an aqueous-alcohol solution, and obtained a mixture of primary and secondary ethers. By using the method of Hughes [7] on substitution reactions, the authors conclude that in absolute alcohol the reaction is of a bimolecular S_N^2 type; in aqueous alcohol solution, of mixed bimolecular S_N^2 and monomolecular S_N^1 types.

Thus, for primary allyl halide isomers all investigators indicate the formation of ethers of the respective alcohols, according to the reaction:



The problem of the action of alkali alcoholate on secondary allyl halide compounds has not been clarified in the literature. Meisenheimer and Link indicate that in this case complex mixtures, containing unsaturated hydrocarbons, are formed; Roberts, Young and Winstein merely refer to the formation of a mixture of primary and secondary ethers.

In our previous investigations dealing with the action of alkali alcoholate on allyl halide isomers by one of us and B. A. Arbuzov [8] it was shown that the nature of the alcohol exerts the main influence on the course of the reaction between the primary allyl halide isomers and alkali alcoholates.

By the action of potassium hydroxide on 1-methoxy-5-chloropentene-4 in a solution of primary and secondary alcohols the corresponding ethers were isolated, and in the case of tertiary butyl alcohol mainly: 1-methoxy-2,4-pentadiene and dimethoxypentenyl ether. By the action of alkali alcoholate on secondary methoxychloropentene the formation of the same 1-methoxy-2,4-pentadiene and of a mixture of ethers, corresponding by structure to primary and secondary alcohols, was shown. The present article covers the action of alkali alcoholate on isomeric butoxychloropentenes. It was found that butoxychloropentenes are more suitable for the investigation of the reactions with alkali alcoholates than are methoxychloropentenes. This is because the resulting products have a considerably higher boiling point than the alcohols used in the reaction, and therefore can be readily and quantitatively isolated. This fact enabled us to obtain new data of

great importance in characterizing these reactions.

As a result of the action of potassium hydroxide on primary butoxychloropentene (1 butoxy 5 chloro 3 pentene) in solutions of methyl, ethyl, n-propyl and n butyl alcohols, ethers of the corresponding alcohols were obtained as the main reaction products. The constants of the ethers are given in the following table:

No.	Name of ethers	Formula	Boiling point	n_D^{20}	d_4^{20}
1	1 Butoxy 5 methoxy 3 pentene	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2$ $\text{OC}_4\text{H}_9 \quad \text{OCH}_3$	93° (9mm)	0.8686	1.4328
2	1 Butoxy-5 ethoxy 3 pentene	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2$ $\text{OC}_4\text{H}_9 \quad \text{OC}_2\text{H}_5$	96 97 (8.5 mm)	0.8677	1.4336
3	1 Butoxy-5 n propoxypentene	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2$ $\text{OC}_4\text{H}_9 \quad \text{OC}_3\text{H}_7$	110 (8mm)	0.8606	1.4342
4	1,5 Di n butoxy 3-pentene	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2$ $\text{OC}_4\text{H}_9 \quad \text{OC}_4\text{H}_9$	121 (16 mm)	0.8583	1.4363

However, in addition to ethers, in the case of propyl alcohol, 1-butoxy 2,4-pentadiene was also isolated in a 5% yield; in the case of n-butyl alcohol, butoxypentadiene was obtained in a yield of 17%, and di butoxypentenyl ether was obtained in a yield of 7%. Carrying out the reaction in a solution of tertiary butyl alcohol gives rise to the following main reactions: 1-butoxypentadiene of m.p. 59-60°C (10 mm), n_D^{20} 1.4490, d_4^{20} 0.8230 was obtained in a yield of 26%, and the dibutoxypentenyl ether, 180-182°C (7 mm), n_D^{20} 1.4538, d_4^{20} 0.9013 was obtained in a yield of 35%. The presence of conjugated double bonds in butoxypentadiene was verified by the reaction with maleic anhydride.

The results obtained confirmed our earlier views as to the mechanism of this reaction and suggested several generalizations. The difference in the course of the reactions between primary butoxychloropentene and potassium hydroxide in methyl, ethyl, propyl, butyl and tertiary butyl alcohols can be interpreted as due to a gradual decrease of the dissociation of the named alcohols giving rise to the formation of a proton and alkoxyl ion, in the order:



The differences in the dissociation of the alcohols follow from the modern presentation of the magnitudes of the inductive effects of alkyl groups.

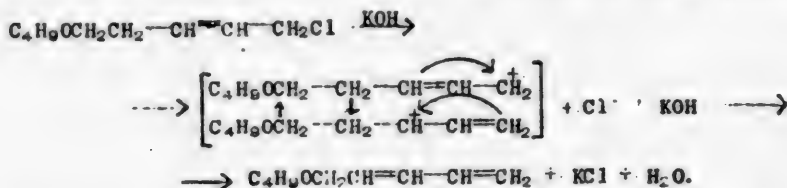
In methyl and ethyl alcohols, due to their considerable dissociation into a proton and alkoxyl anion and the high coordinative capacity of alkoxyl anions as compared with chloride ions, the reactions result in the formation of ethers only, of the bimolecular S_{N}^2 type. The formation of an ethyl ether of the primary alcohol, together with a small amount of alcohol, was also found in the treatment of the chloride with potassium hydroxide in 70% ethyl alcohol; this indicates the considerably high coordinative capacity of the alkoxyl anions as compared with the hydroxyl ions.

In the case of propyl and butyl alcohols, because of their smaller degree of dissociation as compared with methyl and ethyl alcohols, a lower concentration of alkoxyl anions is present in the reaction mixture. As a result, in addition to the formation of ether, there are side reactions leading to the formation of a diene hydrocarbon and dibutoxypentenyl ether. The diene hydrocarbon, together with the ether, was also obtained by us in the treatment of the chloride with butyl alcohol alcoholate in the solution of the same alcohol.

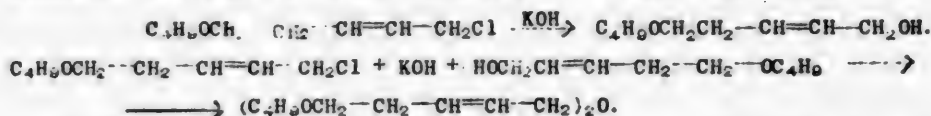
In tertiary butyl alcohol the formation of diene hydrocarbon and dibutoxypentenyl ether represents the main reaction; tertiary butyl alcohol actually plays the part of an inert solvent. In order to prove this a reaction was carried out between potassium hydroxide and primary butoxychloropentene in a dioxane solution; butoxypentadiene and di butoxypentenyl ethers

were also obtained. In the absence of solvent, upon heating the chloride with the powdered potassium hydroxide the reaction proceeds very slowly with the formation of a diene hydrocarbon only.

The formation of a diene hydrocarbon in these experiments is explained as due to the presence of the monomolecular, S_N^1 type, the reaction taking place in part:

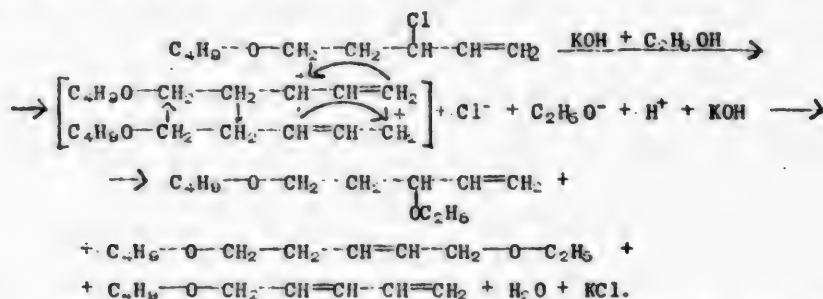


Di-butoxypent-2-enyl ether is formed, apparently according to the scheme:



On the basis of the experimental data it can be concluded that the reactions between potassium hydroxide and primary butoxychloropentene in methyl and ethyl alcohols take place according to bimolecular S_N^2 type; starting with propyl, the reaction of the monomolecular S_N^1 type becomes noticeable, and in tertiary butyl alcohol it predominates.

Interesting results were obtained in the investigation of the action of alkali alcohols on 1-butoxy-3-chloro-4-pentene (secondary chloride). In the reaction between potassium hydroxide and secondary butoxychloropentene in a solution of ethyl alcohol three products were obtained: 1-butoxy-2,4-pentadiene in a yield of 31%, b.p. 59-60°C (10mm), n_D^{20} 1.4505, d_4^{20} 0.8223; ethyl ether of secondary alcohol in a yield of 22%, b.p. 78°C, (10mm), n_D^{20} 1.4280, d_4^{20} 0.8632; and the ethyl ether of the primary alcohol with a yield of about 8%, b.p. 97°C, (10mm), n_D^{20} 1.4340, d_4^{20} 0.8621. Apparently, the reaction with secondary butoxychloropentene takes place to a great extent according to S_N^1 type:



When the reaction was carried out in a solution of butyl alcohol, butoxy-2,4-pentadiene was the main product. This is in agreement with the earlier conclusions as to the nature of the alcohol in determining the course of the reaction between the allyl halide isomers and alkali.

EXPERIMENTAL

The action of KOH on 1-butoxy 5-chloro-3-pentene in a solution of methyl alcohol

7 g. KOH was dissolved in 80 ml. methyl alcohol, and to this solution was added 15 g. of 1-butoxy-5-chloro-3-pentene. The reaction mixture was refluxed for three hours on a water

bath. The precipitated KCl was filtered off. Methyl alcohol was distilled off. The residue diluted with a small amount of water was extracted with ether. The ether extract was dried with calcium chloride, the ether distilled off, the residue fractionated in vacuo by using a Widmer column. Fractionation yielded 9 g. 1-butoxy-5-methoxy-3-pentene.

B.p. 93°C (9mm); n_D^{20} 1.4328; d_4^{20} 0.8686.

Found: MR_D 51.48.

$C_{10}H_{20}O_2$. Calculated: MR_D 51.21.

0.1101 g. substance. 0.2811 g. CO_2 ; 0.1158 g. H_2O .

Found %: C 69.60; H 11.69

$C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.67.

The action of KOH on 1-butoxy-5-chloro-3-pentene in a solution of ethyl alcohol

The reaction was carried out as described in the previous experiment. To a solution of 10 g. KOH in 100 g. ethyl alcohol was added 20 g. of 1-butoxy 5-chloro-3-pentene. The reaction mixture was heated for three hours on a water bath. Fractionation of the reaction mixture yielded 12.7 g. 1-butoxy-5-ethoxy-3-pentene.

B.p. 96-97°C (8.5mm); n_D^{20} 1.4336; d_4^{20} 0.8677.

Found: MR_D 55.80.

$C_{11}H_{22}O_2$. Calculated: MR_D 55.82.

0.1121 g. substance: 0.2908 g. CO_2 ; 0.1196 g. H_2O .

Found %: C 70.71; H 11.85

$C_{11}H_{22}O_2$. Calculated %: C 70.96; H 11.83.

The action of KOH on 1-butoxy-5-chloro-3-pentene in a solution of n-propyl alcohol

9 g. KOH was dissolved in 80 g. n-propyl alcohol and to this solution was added 18 g. of chloride. The mixture was heated on a water bath for three hours. Propyl alcohol was distilled off on a glycerine bath, and finally under a slight vacuum. The residue was diluted with water and extracted with ether. The ether extract was dried with calcium chloride, the ether was distilled off, and the residue distilled in vacuo. Yield: 0.6 g. of 1-butoxy-2,4-pentadiene and 10.8 g. 1-butoxy 5-propoxy-3-pentene.

B.p. 110°C (8mm); n_D^{20} 1.4342; d_4^{20} 0.8606.

Found: MR_D 60.59.

$C_{12}H_{24}O_2$. Calculated: MR_D 60.43.

0.1131 g. substance. 0.2972 g. CO_2 ; 0.1220 g. H_2O .

Found %: C 71.81; H 11.97.

$C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00

The action of KOH on 1-butoxy-5-chloro-3-pentene in a solution of n-butyl alcohol

To a solution of 20 g. KOH in 200 g. butyl alcohol was added 30 g. 1-butoxy-5-chloro-3-pentene. The mixture was heated for 2 hours on a water bath. Butyl alcohol was distilled off from a flask provided with a Widmer column under a pressure of 150 mm. The residue was treated with water and extracted with ether. After distilling off the ether the residue was distilled in vacuo. The following fractions were collected:

1. B.p. 62-100° (9mm); wt. 6.5 g.

2. B.p. 102-160° (9mm); wt. 12.7 g.

3. B.p. 165-180° (9mm); wt. 1.9 g.

Repeated fractionations yielded: 4.2 g. 1-butoxy 2,4-pentadiene; b.p. 65°C (13mm), n_D^{20} 1.4520; 10.3 g. 1,5-di-butoxy 3-pentene; b.p. 116°C (10mm), n_D^{20} 1.4352, and 1.3 g. di-butoxypentenyl ether; b.p. 180°C (7mm), n_D^{20} 1.4535.

Action of KOH on 1-butoxy-5-chloro-3-pentene
in a solution of tertiary butyl alcohol

To a solution of 10 g. KOH in 120 g. of tertiary butyl alcohol was added 20 g. of primary chloride. The mixture was heated on a water bath for four hours.

Tertiary butyl alcohol was distilled off on an oil bath from a flask fitted with a Widmer column. The residue was treated with water and ether. Fractionation of the reaction products yielded:

1. B.p. 56-62°C (9mm); wt. 5.7 g.
2. B.p. 63-168° (5mm); wt. 5.2 g.
3. B.p. 169-182° (5mm); wt. 6.4 g.

A second distillation of the first fraction yielded 4.7 g. 1-butoxy-2,4-pentadiene; b.p. 59-60° (10mm), n_D^{20} 1.4490, d_4^{20} 0.8230; third fraction - 5.9 g. dibutoxypentenyl ether:

B.p. 180-182°C (7mm); n_D^{20} 1.4538; d_4^{20} 0.9013.
Found: MR_D 89.50
 $C_{18}H_{34}O_3F_2$. Calculated: MR_D 89.32.

0.1018 g. substance: 0.2696 g. CO_2 ; 0.1053 g. H_2O .
Found %: C 72.22; H 11.49
 $C_{18}H_{34}O_3$. Calculated %: C 72.48; H 11.41.

Repeated fractionation of the second fraction failed to yield a compound of constant boiling point.

Action of KOH on 1-butoxy-5-chloro-3-pentene
in a dioxane solution

A mixture of 14 g. KOH and 27 g. primary chloride in 200 g. dioxane was heated on a boiling water bath for 9 hours.

Dioxane was distilled off from a flask fitted with a Widmer column, the residue diluted with water and extracted with ether. After distilling off the ether the residue was fractionated in vacuo. The following fractions were collected:

1. B.p. 77-90°C (23mm), wt. 8 g.
2. B.p. 110-111° (19 mm), wt. 12.5 g.
3. B.p. 180-200° (10mm), wt. 2.3 g.

A repeated fractionation of the first fraction yielded 6 g. 1-butoxy-2,4-pentadiene, b.p. 67°C (15mm), n_D^{20} 1.4534; d_4^{20} 0.8210. Fractionation of the third fraction yielded 1 g. dibutoxypentenyl ether, b.p. 185°C, n_D^{20} 1.4541. Second fraction -- recovered chloride.

Action of KOH on 1-butoxy-5-chloro-3-pentene
in a solution of 70% ethyl alcohol

10 g. KOH was dissolved in 100 g. 70% ethyl alcohol, and 20 g. of chloride added to the solution. The mixture was heated on a water bath for 3 hours. After distilling off the ethyl alcohol the contents separated into two layers. The top layer was separated, and the bottom layer was extracted with ether. The ether extract was added to the top layer. After distilling off the ether the residue was fractionated in vacuo from a flask fitted with a spiral Widmer column. Yield 11.8 g. 1-butoxy-5-ethoxy-3-pentene, b.p. 107-109°C (14mm). n_D^{20} 1.4340, d_4^{20} 0.8677 and about 2 g. 1-butoxy-3-pentene-5-ol.

B.p. 125-126°C (15mm); n_D^{20} 1.4487; d_4^{20} 0.9093.
Found: MR_D 46.79
 $C_9H_{18}O_2F_1$. Calculated: MR_D 46.46.

**Action of butyl alcohol alcoholate on 1-butoxy-5-chloro-3-pentene
in a solution of absolute butyl alcohol**

5.5 g. metallic sodium was dissolved in 195 g. absolute butyl alcohol. To this solution was added 40 g. of 1-butoxy-5-chloro-3-pentene. The mixture was heated on a water bath for 4 hours. The alcohol was distilled off, the residue diluted with water, and treated with ether. One fractionation of the reaction products yielded 14.5 g. 1-butoxy-3,4-pentadiene and 8.2 g. of a fraction boiling in the range 117-135°C (16 mm), which on repeated fractionation yielded 0.2 g. 1,5-dibutoxy-3-pentene.

b.p. 121° (16mm); n_D^{20} 1.4363; d_4^{20} 0.8583.

Found: MR_D 64.77.
 $C_{13}H_{26}O_2F_2$ Calculated MR_D 65.05.

**Action of KOH on 1-butoxy-5-chloro-3-pentene
in the absence of a solvent**

A mixture of 9 g. chloride and 5 g. of powdered KOH was heated on a water bath for 7 hours. The mixture was treated with water and extracted with ether. The ether extract was dried with calcium chloride, the ether was distilled off, and the residue was fractionated in vacuo. Yield 0.8 g. butoxypentadiene and 6.5 g. of initial chloride.

**Action of KOH on 1-butoxy-3-chloro-4-pentene
in a solution of ethyl alcohol**

20 g. KOH was dissolved in 120 g. ethyl alcohol. To the solution was added 40 g. of 1-butoxy-3-chloro-4-pentene. The mixture was heated on a water bath for three hours. The precipitate of potassium chloride was filtered off (14 g. KCl, theoretical amount 16.8 g.). Ethyl alcohol was distilled off. The residue was treated with a small amount of water and extracted with ether. The ether extract was dried with calcium chloride, the ether distilled off, and the residue fractionated in vacuo from a flask provided with a spiral Widmer column. The following fractions were collected:

1. B.p. 57-65°C (10mm). n_D^{20} 1.4509, 13.0 g.
2. B.p. 76-96°C (10mm). n_D^{20} 1.4290, 12.7 g.
3. B.p. 96-97°C (10 mm) n_D^{20} 1.4345, 3.2 g.

Repeated fractionation of the first fraction yielded 10.2 g. 1-butoxy-2,4-pentadiene:

B.p. 59-60°C (10mm); n_D^{20} 1.4505, d_4^{20} 0.8223

Found MR_D 45.81

$C_9H_{18}O$ F_2 . Calculated MR_D 44.47; exaltation 1.34

0.1241 g. substance: 0.3238 g. CO_2 ; 0.1350 g. H_2O .

Found %: C 76.98; H 11.42.

$C_9H_{18}O$. Calculated %: C 77.14; H 11.43.

Fractionation of the second fraction yielded 9.3 g. 1-butoxy-3-ethoxy-4-pentene:

B.p. 73°C (10mm); n_D^{20} 1.4280; d_4^{20} 0.8632.

Found MR_D 55.44.

$C_{11}H_{22}O_2$ F_2 . Calculated MR_D 55.82.

0.1250 g. substance: 0.3238 g. CO_2 ; 0.1350 g. H_2O .

Found %: C 70.64; H 12.00

$C_{11}H_{22}O_2$. Calculated %: C 70.96; H 11.83.

Third fraction - 1-butoxy-5-ethoxy-3-pentene.

Addition of 1-butoxy-2,4-pentadiene to maleic anhydride

2 g. of maleic anhydride and 3 g. of 1-butoxy-2,4-pentadiene were heated in a flask over the flame of an alcohol burner. A violent reaction occurred. Fractionation of the reaction product yielded 1.6 g. of a substance, b.p. 192° (13mm). Addition product -- a thick liquid of light yellow color, gives no crystals on standing.

0.1163 g. substance: 0.2787 g. CO₂; 0.0775 g. H₂O.
Found %: C 65.35; H 7.60.
C₁₃H₁₈O₄. Calculated %: C 65.55; H 7.56.

CONCLUSIONS

1. An investigation has been made of the action of KOH on 1-butoxy-5-chloro-3-pentene, in a solution of methyl, ethyl, n-propyl, n-butyl and tertiary butyl alcohols. In methyl and ethyl alcohols the reactions follow a bimolecular S_N² type with the formation of ethers. In the other alcohols, in addition to ethers, 1-butoxy-2,4-pentadiene and dibutoxypentenyl ether are formed. Tertiary butyl alcohol plays mainly the part of a solvent. An interpretation of the reaction mechanism based on the concepts of electronic theory has been given.

2. It has been shown that the reaction between KOH and secondary butoxychloropentene in ethyl alcohol solution follows both S_N¹ and S_N² types with the formation of 1-butoxy-2,4-pentadiene and a mixture of ethyl ethers, corresponding by structure to primary and secondary alcohols.

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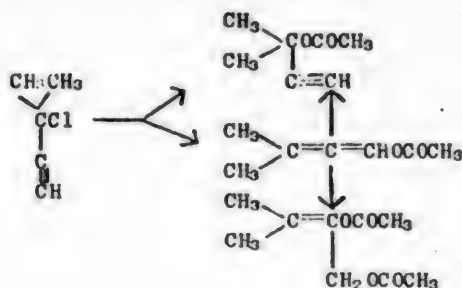
INTRAMOLECULAR REARRANGEMENTS IN THE ACETYLENE SERIES

IV. ACTION OF 3-CHLORO-3-METHYLPENTYNE-1 and 3-CHLORO-3-METHYLHEXYNE-4 WITH SILVER ACETATE

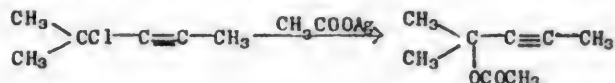
A. I. Zakharova

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Chemical Faculty of Leningrad State University

In previous communications [1, 2] it has been shown that in the reaction of tertiary acetylene chlorides, obtained from the corresponding alcohols by the action of halogenating agents, with silver acetate in the presence of glacial acetic acid, the initial chloride plays the main role. The presence of a free acetylenic hydrogen yields three substances in the reaction with silver acetate: the acetate of the initial carbinol, which represents a normal reaction product; the acetate of allene structure formed as a result of an intramolecular rearrangement at the moment of reaction; and ethylene diacetate. It has been established that allene acetate is unstable and when heated in glacial acetic acid is isomerized to a stable acetate of an acetylenic structure. It has also been shown that, under the conditions of the reaction allene acetate adds to itself a molecule of acetic acid forming the diacetate.



Entirely different results were obtained when the initial substance in the reaction with silver acetate was a chloride, with a methyl group in place of the free acetylenic hydrogen. It has been shown: first, that such a chloride can be prepared more readily by the action of hydrogen chloride on the carbinol; second, in the reaction of the chloride with silver acetate in the presence of glacial acetic acid the only reaction product is the acetate, corresponding to the initial carbinol.



It was of interest to see whether the same observations would be made as in earlier investigation by using other tertiary acetylenic chlorides with silver acetate. For this purpose a study has been made of the reaction between silver acetate and 3-chloro-3-methyl-1-pentyne (II) and 3-chloro-3-methyl-4-hexyne (VII).

I. The reaction between 3-chloro-3-methyl-1-pentyne (II) and silver acetate in the presence of glacial acetic acid took place rapidly, exothermically, without tarring or changing color, resulting in the formation of a mixture of products of which three substances were isolated and characterized.

The substance with a b.p. of 85-86°C at 75 mm formed a white precipitate with ammoniacal silver oxide, and added two hydrogen molecules during hydrogenation.

The determinations of molecular weight and elementary compositions have shown that this substance is an acetate. The sharp boiling point, and also the closeness of its physical constants to those of the acetate 3-aceto-methyl-1-pentyne (III), obtained by the action of acetic anhydride on methyl ethyl-acetylenyl-carbinol (I) indicate that it is an homogeneous substance a product of the normal substitution of chlorine in the chloride by an acetyl group.

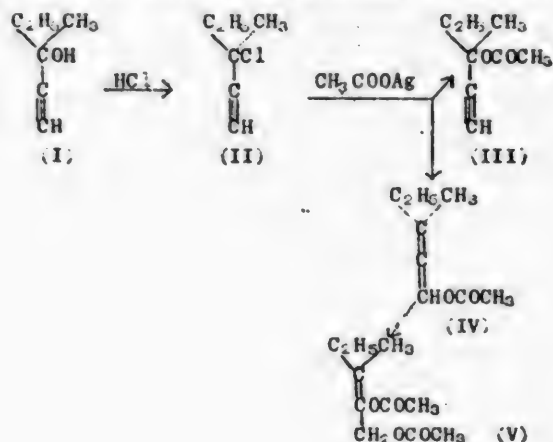
The substance of b.p. 90-91°C at 30 mm. has a sharper odor than the acetylenic acetate; it has the same elementary composition. It gives no reaction for free acetylenic hydrogen; during hydrogenation it also adds two hydrogen molecules, forming a saturated acetate, resembling in odor isoamyl acetate ether. All these data suggest as the structure of the isomeric acetate an allene type structure: 1-aceto-3-methyl-1,2-pentadiene (IV).

The third reaction product has a b.p. of 108-110°C at 12 mm. When hydrogenated it adds one hydrogen molecule. On oxidation, it yields methylethylketone and oxalic acid. The data for analysis of the elements, determination of the molecular weight and physical constants, and also the results on oxidation suggest a structure for this compound of: 1,2 diaceto 3 methyl-2-pentene (V).

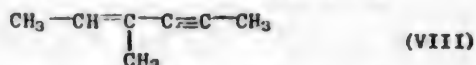
Since methods of formation of similar substances have been exhaustively studied using as an example the action of silver acetate on the chloride obtained from dimethylacetylenyl-carbinol (I), the following observation can be made in this case. It has been established by definite experiments that the acetylenic acetate was stable and was not isomerized to an allene acetate when heated in glacial acetic acid.

The allene acetate was unstable and under experimental conditions was changed in two directions. It was isomerized to an acetate of acetylenic structure and also added another molecule of acetic acid, changing to the diacetate.

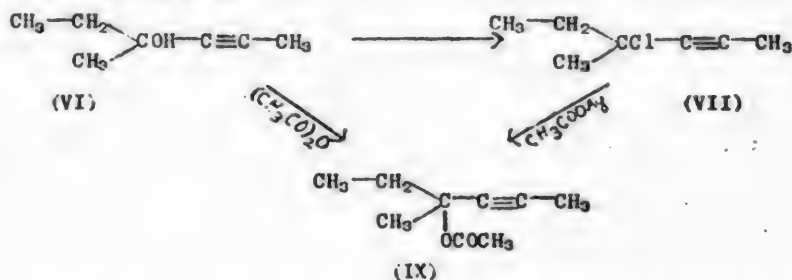
Thus, for this example, interesting transformations have been observed which could be explained only by assuming that the formation of the anomalous reaction product of allene acetate occurred as a result of an intramolecular rearrangement at the moment of the reaction; i.e., this is not a result of a subsequent isomerization of the first normal reaction product - acetylenic acetate. This can be expressed by the following scheme:



II. The reaction between the chloride -- 3-chloro-3-methyl-4-hexyne (VII), with a methyl group adjacent to the triple bond in place of a free acetylenic hydrogen, is entirely different. Preparation of the chloride; as pointed out in an earlier communication [2] the chloride can be obtained very readily in the reaction of dimethyl-methylacetylenyl-carbinol with hydrogen chloride. The chloride is also obtained in a good yield in the reaction of methylethyl methylacetylenyl-carbinol (VI) with hydrogen chloride. It is true that this reaction is somewhat complicated by the simultaneous dehydration of carbinol (VI) with the formation of the hydrocarbon -- 3-methyl-2-hexene-4-yne.



The structure of the latter was proved by oxidation, which yielded acetic acid only. To avoid losses in the preparation of chloride it was found more desirable to treat methyl-ethyl-methylacetylenyl-carbinol with phosphorous trichloride in an ether solution. In the last case the yield of the chloride (VII) was increased. The reaction between 3-chloro-3-methyl-4-hexyne (VII) with silver acetate in the presence of glacial acetic acid took place rapidly, exothermically; however, after a corresponding treatment of the reaction product, only one substance, b.p. 69-70°C at 15 mm, was isolated. According to analysis it corresponded to the acetate (IX) and was identical with the acetate obtained by heating the carbinol (VI) with acetic anhydride.



Thus, in this case, as in the earlier investigation [2], no products were found which would indicate the presence of an intramolecular rearrangement during the reaction. It is possible that this may be explained by an increase in the mobility of the substituting atom, in this case, chlorine. The introduction of the methyl group with its positive inductive effect into the α -position with respect to the triple bond had pronounced effects

on the properties of the compound of the type $\begin{array}{c} \text{R} \\ | \\ \text{C}^*-\text{C}\equiv\text{C}-\text{CH}_3 \\ | \\ \text{R} \end{array}$: the mobility of the atom at the tertiary carbon was greatly increased. In this respect, of particular interest were the results obtained on the hydrogen chloride treatment of the acetylene tertiary alcohol, of the type mentioned above, where R is a tertiary butyl group. The results of this investigation will be given in detail in a communication in the near future. Here it will be pointed out that, as shown by our experiments, the presence of a methyl group in the α -position with respect to the triple bond completely disproves the assertion found repeatedly in the literature [5] that compounds containing a neopentyl group are inert in the reaction of substitution of chlorine for hydroxyl and in the reaction of saponification of the chloride obtained in this case.

EXPERIMENTAL

1. Reaction between acetylenic chloride -- 3-chloro-3-methyl-1-pentyne (II) and silver acetate.

The initial compounds for this reaction were prepared as follows:

Methylethyl acetylenyl carbinol (I) was prepared by the method of A.E. Favorsky [4], as described earlier [5], from methylethylketone and acetylene in the presence of powdered

potassium hydroxide in ether. Numerous experiments, carried out in the Favorsky laboratory, on the preparation of tertiary acetylenic alcohols resulted in a significant improvement in this method. The passage of acetylene directly into the mixture from a cylinder under pressure and the use of a rapidly rotating metallic stirrer with wide blades, provided efficient mixing of the reaction mixture, and decreased considerably the amounts of ether and powdered potassium hydroxide introduced into the reaction. Thus, the formulation [6] including the amounts of the initial materials, could be modified. By observing the conditions mentioned above, the reaction could be carried out by taking 600-750 ml. ether per 2 g.-mol of ketone in place of 1.5 l. ether, and 200-250 g. of powdered alkali in place of 350 g. The reaction cylinder was cooled externally with ice. Considering the reversibility of the reaction of formation of tertiary acetylenic alcohols from ketones and acetylenic hydrocarbons in the presence of KOH in absolute ether, confirmed earlier [7], it is recommended that the entire process be completed in one day. According to its physico-chemical constants, the properties of the carbinol were identical with those determined earlier [8].

3-Chloro-3-methyl-1-pentyne (II) was obtained by treating the carbinol for 4 hours with hydrochloric acid (d 1.19), in the presence of CuCl_2 and NH_4Cl [6]. For 100 g. of carbinol were taken 170 ml. of hydrochloric acid, 20 g. of CuCl_2 and 10 g. of NH_4Cl . The b.p. of the chloride was 49-50°C at 100 mm. and the physical constants were identical with those determined earlier [6].

To 42 g. (1/4 g.-mol) CH_3COOAg in 50 ml. of glacial acetic acid with efficient stirring was added dropwise a solution of 29 g. (1/4 g.-mol) of chloride in 25 ml. glacial acetic acid. Heat was evolved during the addition of chloride. The mixture was heated with stirring on a water bath at 60°. On cooling, the reaction mixture was diluted with water, the acid was neutralized with 10% soda solution and the reaction products extracted with ether; the ether extract was dried, and the ether distilled off. As a result of 2 experiments, 91.56 g.-mol. of chloride yielded 42 g. of a mixture of acetates (60% of theoretical). Fractionation yielded the following fractions:

1.	b.p.	to 85°C	at 75 mm.	4 g.
2.	b.p.	85-86	at 75 mm.	15 g.
3.	b.p.	87-89	at 30 mm.	4 g.
4.	b.p.	90-91	at 30 mm.	8 g.
5.	b.p.	92-107	at 12 mm.	2 g.
6.	b.p.	108-110	at 12 mm.	3 g.

Acetylenic acetate --- 3-aceto-3-methyl-3-methyl-1-pentyne (III). B.p. 85-86°C at 75 mm (fraction 2) had a weak ethereal odor, gave a positive reaction for acetylenic hydrogen with an ammoniacal solution of silver oxide.

$$d_4^{20} 0.9477; d_4^{20} 0.9286; n_D^{20} 1.42219; n_D^{20} 1.43039; n_D^{20} 1.42459.$$

Found: MR_α 38.33; MR_β 38.98; MR_γ 38.51.

$\text{C}_{10}\text{H}_{16}\text{O}_2$ F. Calculated: MR_α 38.46; MR_β 39.16; MR_γ 38.67.

0.1534 g. substance. 21.02 g. benzene: Δt 0.27°C.

Found: M 135.14.

$\text{C}_{10}\text{H}_{16}\text{O}_2$. Calculated: M 140.

0.1401 g. substance. 0.3523 g. CO_2 ; 0.1082 g. H_2O .

Found %: C 68.58; H 8.64.

$\text{C}_{10}\text{H}_{16}\text{O}_2$. Calculated %: C 68.57; H 8.57.

In the hydrogenation in an ether solution in the presence of platinum black 5 g. of acetate absorbed 1.6 l. hydrogen, i.e. the theoretical amount required when calculated for 1 triple bond.

The acetate (III) was prepared for comparison by heating 10 g. of methylethylacetylenyl carbinol (I) with 50 g. acetic anhydride on a water bath for 6 hours. B.p. 85-86°C at 75 mm. n_D^{20} 1.42460.

Allene acetate 1 aceto-3-methyl-1,2-pentadiene (IV). B.p. 90-91°C at 30 mm.,

(fraction 4) had a penetrating, but pleasant, ethereal odor, differing greatly from the odor of acetylenic acetate described above; it gave no reaction for free acetylenic hydrogen.

d_4^{20} 0.9859; d_4^{20} 0.9672; n_D^{20} 1.45784; n_D^{20} 1.46812; n_D^{20} 1.46088.

Found: MR_{α} 39.48; MR_{β} 40.22; MR_D 39.71.

$C_6H_{12}O_2F_2$. Calculated: MR_{α} 39.49; MR_{β} 40.31; MR_D 39.74.

0.1932 g. substance: 14.85 g. benzene: Δt 0.46°.

Found: M 141.41.

$C_6H_{12}O_2$. Calculated: M 140.

0.0788 g. substance: 0.1972 g. CO_2 : 0.0616 g. H_2O .

0.0866 g. substance: 0.2169 g. CO_2 : 0.0684 g. H_2O .

Found %: C 68.25; 68.21; H 8.74, 8.83.

$C_6H_{12}O_2$. Calculated %: C 68.57; H 8.57.

In hydrogenation in an ethereal solution in the presence of platinum black 2 g. of acetate absorbed 0.63 l. of hydrogen; 0.64 l. represents the theoretical amount when calculated for 2 double bonds. After distilling off the ether there remained a small amount of substance, with an odor resembling that of isoamyl acetic ether.

Ethylene diacetate - 1,2-diaceto 3-methyl-2-pentene (V). B.p. 108-110°C at 12 mm (fraction 5). isolated in a small amount (3 g.), gave a negative reaction for acetylenic hydrogen.

d_4^{20} 1.0377; d_4^{20} 1.0185; n_D^{20} 1.43812; n_D^{20} 1.44734.

Found: MR_{α} 51.54; MR_{β} 52.48.

$C_{10}H_{16}O_4F$. Calculated: MR_{α} 50.94; MR_{β} 51.83.

0.2112 g. substance: 17.40 g. benzene: Δt 0.32°C.

Found: M 189.6

$C_{10}H_{16}O_4$. Calculated: M 200.

0.0995 g. substance: 0.2101 g. CO_2 : 0.0780 g. H_2O .

0.1327 g. substance: 0.2725 g. CO_2 : 0.0973 g. H_2O .

Found %: C 60.00, 60.07; H 8.20, 8.27.

$C_{10}H_{16}O_4$. Calculated %: C 60.0; H 8.0

The presence of one double bond was verified by the hydrogenation of diacetate in an ether solution in the presence of platinum black. 0.5 g. diacetate absorbed 60 ml. hydrogen. When calculated for one double bond the amount of hydrogen required was 56 ml.

To verify the structure of the diacetate 2 g. of the latter was oxidized with 1% alkaline $KMnO_4$ solution, with cooling. When no more discoloration occurred in the cold, the oxidation was discontinued, and the MnO_2 precipitate filtered off. The remaining solution was boiled to remove the neutral oxidation products which were then collected in the receiving flask with the acetate solution of p nitrophenylhydrazine. A precipitate of p-nitrophenylhydrazone was formed which after recrystallization from methanol had a m.p. of 126-127°C. A mixture with p nitrophenylhydrazine of methylethyl ketone melted at 127°C.

0.0489 g. substance: 8.8 ml. N_2 (25°C, 762.6 mm)

0.0418 g. substance: 7.5 ml. N_2 (25°C, 762.5 mm)

Found %: N 20.29, 20.23.

$C_{10}H_{16}O_2N_3$. Calculated %: N 20.29.

The residual solution was concentrated, then neutralized with sulfuric acid. The free organic acids were first extracted with ethyl ether; then the water layer was extracted with ethyl acetate. Distilling off the ethyl acetate, the mixture yielded a small amount of crystals, m.p. from a mixture of acetone and benzene 99-101°C. A mixture with oxalic acid showed no depression on melting.

Distilling off the ether, the mixture yielded a substance with an acetic acid odor. The silver salt of the acid had the composition of silver acetate.

2. Reaction between acetylenic chloride -- 3-chloro-3-methyl-4-hexyne (VII) and silver acetate.

1. Preparation of methylethyl-methylacetylenyl-carbinol (VI)

The carbinol was prepared by the method of A. E. Favorsky from methylethylketone and allylene in the presence of powdered KOH in ether solution. In order to avoid the loss of methylacetylene, a product obtainable with difficulty, the usual method of preparation of carbinol was somewhat modified. In a three-necked flask provided with a rapidly rotating mechanical stirrer was charged 200 g. of powdered KOH and 400 ml. of ether. The mixture was cooled to 0°C and saturated with methylacetylene. Then by stirring very rapidly and cooling, methylethylketone (1.5 g. mol.; in 200 ml ether was added in two portions; first, half the amount, and after 1.5-2 hours, the remaining portion. Thus, the concentration of the ketone in the reaction mixture remained always high, the absorption of methylacetylene was rapid, and the entire process of preparation of carbinol was completed in 6 hours. Upon completion of the reaction, the mixture was decomposed with ice-water, the ether layer separated, dried with Na_2SO_4 , and the remaining product was fractionated in vacuo. The yield of carbinol by using this method attained 80% of theoretical.

B.p. 92-92.5°C at 100 mm; d_4^{20} 0.8942; d_4^{20} 0.8759; n_D^{20} 1.44797; n_D^{20} 1.4536; n_D^{20} 1.45431.

Found. MR_D 34.22; MR_α 34.05; MR_β 34.64.

$\text{C}_8\text{H}_{12}\text{O}$. Calculated. MR_D 34.16; MR_α 33.96; MR_β 34.60.

0.1248 g. substance; 25.73 g. benzene; Δt 0.22°.

Found. M 110.23;

$\text{C}_8\text{H}_{12}\text{O}$. Calculated: M 112.

0.3930 g. substance: 0.2549 g. CO_2 ; 0.0931 g. H_2O .

0.0976 g. substance: 0.2660 g. CO_2 ; 0.0974 g. H_2O .

Found %: C 74.75, 74.58; H 11.12, 11.16.

$\text{C}_8\text{H}_{12}\text{O}$. Calculated %: C 75.00; H 10.71.

2. Action of hydrogen chloride on carbinol (VI).

Hydrogen chloride, prepared by heating concentrated hydrochloric acid, was introduced into carbinol. First, there was a complete absorption of the gas, the temperature of the mixture gradually rising; at 80-85°C the reaction was violent, the absorption of hydrogen chloride stopped, and the mixture separated into two layers. The bottom water layer was separated, the reaction product dried with calcium chloride and fractionated. The following fractions were obtained:

1. B.p. 55-65°C at 100 mm -- 12 g.

2. B.p. 66-70 at 100 mm -- 10 g.

3. B.p. 71-76 at 100 mm -- 25 g.

The first and second fractions were combined and fractionated. The product had a wide boiling point range (55-68°C at 100 mm), a characteristic hydrocarbon odor, but gave a distinct reaction for the presence of halogen. In order to free the product from halogen it was heated with metallic sodium for several hours and then fractionated over sodium. The product obtained was hydrocarbon (VIII), a colorless mobile liquid with a penetrating odor.

B.p. 107-108°C at 737 mm. d_4^{20} 0.7944; d_4^{20} 0.7783; n_D^{20} 1.45057; n_D^{20} 1.44691; n_D^{20} 1.45980.

Found. MR_D 32.50; MR_α 32.27; MR_β 33.07.

C_8H_{10} . Calculated: MR_D 32.05; MR_α 31.82; MR_β 32.54.

0.2829 g. substance; 22.02 g. benzene; Δt 0.675°.

Found. M 95.18.

C_8H_{10} . Calculated: M 94.0

0.0737 g. substance: 0.2410 g. CO_2 ; 0.0716 g. H_2O .

0.1011 g. substance: 0.3300 g. CO_2 ; 0.0988 g. H_2O .

Found %: C 89.18, 89.11; H 10.86, 10.93.

C_8H_{10} . Calculated %: C 89.36; H 10.63.

Oxidation of hydrocarbon (VIII). 4 g. of the hydrocarbon was oxidized by using 1% KMnO_4 solution with cooling. The discoloration of the solution stopped after the addition of the calculated amount of KMnO_4 . The MnO_2 precipitate was filtered off. When the salt

solution having an alkaline reaction was heated, no neutral products were found in the distillate. The remaining salt solution was acidified with sulfuric acid, and the organic acids distilled off with steam. Four fractions, 15 ml. each, were collected. All fractions, when heated with Ag_2CO_3 , gave silver salts corresponding in composition to the salts of acetic acid. The absence of formic acid in the oxidation products of the hydrocarbon indicates that the dehydration of methylethyl-methylacetylenyl-carbinol (VI) proceeds only in one direction: at the expense of the CH_2 group with the formation of 3-methyl-2-hexene-4-yne (VIII).

The substance of b.p. $71-76^\circ\text{C}$ at 100 mm. (fraction 3) was again subjected to careful fractionation. The chloride (VII) collected appeared as a colorless, mobile liquid, darkening on standing. When shaken with aqueous AgNO_3 it gave precipitate of AgCl .

B.p. 74°C at 100 mm: d_4^{20} 0.9444; d_4^{20} 0.9253; n_D^{20} 1.44097; n_D^{20} 1.43902; n_D^{20} 1.44995.

Found: MR_D 37.26; MR_X 37.09; MR_B 37.89.
 $\text{C}_7\text{H}_{11}\text{ClF}$. Calculated: MR_D 37.39; MR_X 37.16; MR_B 37.88.

0.2425 g. substance: 15.55 g. benzene: Δt 0.62° .

Found: M 125.75.

$\text{C}_7\text{H}_{11}\text{Cl}$. Calculated: M 130.5.

Found %: Cl 27.05.

$\text{C}_7\text{H}_{11}\text{Cl}$. Calculated %: Cl 27.20.

3. Action of phosphorous trichloride on carbinol (VI)

To 28 g. of carbinol (0.25 g.-mol), dissolved in 50 ml. dry ether, was added slowly, with cooling, 11.4 g. of PCl_3 in 50 ml. of ether. The mixture was maintained for an hour at 0°C , then for 2 hours at room temperature. The heavy layer of phosphoric acid formed on the bottom was separated, the ether layer was washed several times with ice-water, dried with CaCl_2 , and the ether distilled off. The residue was distilled in vacuo (100 mm). It represented a separate substance of b.p. 74°C , having constants identical with those of chloride (VI), obtained by the action of hydrogen chloride on the carbinol. Dehydration of the carbinol with the formation of hydrocarbon (VIII) was scarcely observed in this reaction. The yield of chloride -- 3-chloro-3-methyl-4-hexyne (VII) amounted to 70%.

4. Preparation of methylethyl-methylacetylenyl-carbinol (IX)

a) In a vessel provided with a stirrer were placed 42 g. (0.25 g.-mol) of CH_3COOAg and 50 ml. of glacial acetic acid. To the solution was added dropwise with rapid stirring, a solution of 32.5 g. (0.25 g.-mol) of chloride (VIII) in 25 ml. glacial acetic acid. Evolution of heat was observed. The mixture was heated, with stirring, on a water bath at 60°C , for 4 hours, and diluted with water; the acid was neutralized with 10% soda solution, and the reaction product extracted with ether. The residue, after distilling off the ether, was fractionated.

B.p. $69-70^\circ$ at 15 mm: d_4^{20} 0.9462; d_4^{20} 0.9278; n_D^{20} 1.44045. n_D^{20} 1.43797.

Found: MR_D 43.77; MR_X 43.57.
 $\text{C}_8\text{H}_{14}\text{O}_2$ F. Calculated: MR_D 43.28; MR_X 43.04.

0.1061 g. substance: 25.76 g. benzene: Δt 0.14° .

Found: M 147.12.

$\text{C}_8\text{H}_{14}\text{O}_2$. Calculated: M 154.0.

1586 g. substance: 0.4070 g. CO_2 : 0.1316 g. H_2O .

0.0792 g. substance: 0.2036 g. CO_2 : 0.0660 g. H_2O .

Found %: C 69.93, 70.11; H 9.28, 9.32.

$\text{C}_8\text{H}_{14}\text{O}_2$. Calculated %: C 70.13; H 9.09.

b) A mixture of 15 g. carbinol and 75 ml. of acetic anhydride was heated on a sand bath for 6 hours, cooled and diluted with water. The top ether layer was separated, washed several times with water, dried with Na_2SO_4 , and fractionated. Product -- methylethyl-methylacetylenyl carbinol (3 aceto 3-methyl-4-hexyne) acetate, with constants identical with those obtained for the reaction product of CH_3COOAg and 3-chloro-3-methyl-4-hexyne (section a).

CONCLUSIONS

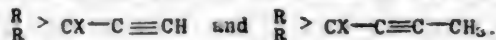
A study has been made of the reaction between silver acetate and two tertiary acetylenic chlorides: 3-chloro-3-methyl-1-pentyne (II) and 3-chloro-3-methyl-4-hexyne (VII), in the presence of glacial acetic acid.

It has been shown that the reaction with chloride (II) is accompanied by intramolecular rearrangement, resulting in the formation of three products: methylethyl-acetylenyl carbinol acetate (III), which is a normal reaction product; an acetate of allene structure - 1-aceto-3-methyl-1,2-pentadiene (IV), and ethylene diacetate (V). It has been proved that the allene acetate (IV) is unstable and when heated in glacial acetic acid is isomerized to an acetylenic acetate (III).

It has been established that in the reaction of the chloride (VII) with silver acetate only an acetate of normal structure - 3-aceto-3-methyl-4-hexyne (IX), is formed. No formation of an isomeric acetate of allene structure has been observed.

In addition, the following new substances were synthesized and characterized: methylethyl-methylacetylenyl-carbinol (VI) by the method of A.E. Favorsky from methyl acetylene and methylethyl ketone, the chloride (VII) by treating the carbinol with phosphorous trichloride. The same chloride was obtained by the action of hydrogen chloride on carbinol and it was established that the reaction was accompanied by a partial dehydration. A enyne hydrocarbon - 3-methyl-2-hexene-4-yne (VIII) was separated and characterized.

Confirmation has been made of an earlier observation that the substitution of a hydrogen atom at the triple bond by a methyl group increases the mobility of the substituents (halogen, hydroxyl), located at the tertiary carbon in compounds of the type:



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PREPARATION OF 1-CHLORO-2-FLUOROETHANE

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No data on 1-chloro-2-fluoroethane have been published in the chemical literature. Therefore it was considered of interest to describe a method of its preparation, and to list some of its physico-chemical properties.

At first an attempt was made to obtain 1-chloro 2-fluoroethane by the Dumas-Fremy method [1] in which dichlorodiethylsulfate is reacted with potassium fluoride. However, the yields were very low. Considerably better results were obtained by reacting the 2-chloroethyl ester of benzenesulfonic acid with potassium fluoride.

As early as 1897, Kastle [2] in an investigation of the ester of benzenesulfonic acid, found that in the presence of salts of hydrogen halide acids, this hydrolysis was complicated by a side reaction of formation of alkyl halides at the expense of the reaction between the ester and the halogen ion:



Later, this reaction was investigated in greater detail by Praetorius [3] for the case of the methyl ester of benzene sulfonic acid, and by McCleary [4] for the ethyl ester of p-toluenesulfonic acid.

In 1925 Peacock [5] applied the reaction between methyl and ethyl esters of p-toluenesulfonic acid and potassium iodide for the preparation of methyl and ethyl iodide. Finally, in 1926 Rodionov [6] investigated the reaction of the esters of toluene sulfonic acid and aqueous potassium iodide and bromide and showed that by using concentrated solutions of these salts the reaction of the formation of alkyl halide predominates and may be employed as a convenient method for the preparation of alkyl bromides and iodides.

It was decided to investigate the behavior of the esters of aromatic sulfonic acids in the presence of salts of hydrofluoric acid, and to see whether this reaction could be employed as a convenient method for the preparation of alkyl fluorides, and particularly for the preparation of chlorofluoroethane.

Experiments with 2-chloroethyl ester of benzene sulfonic acid and potassium fluoride have shown that by applying a concentrated aqueous solution of potassium fluoride and by heating the reaction mixture to boiling, no noticeable reaction was produced. When the 2-chloroethyl ester of benzenesulfonic acid was heated with solid anhydrous potassium fluoride to a temperature of about 190°C. 1-chloro-2-fluoroethane was obtained in a yield of about 35% of theoretical. Dichloroethane was obtained as a by-product. Considerably better results were obtained by heating the ester with concentrated aqueous potassium fluoride in an autoclave at a temperature of 130-150°C. The yield of 1-chloro 2-fluoroethane in this case attained 60% of theoretical, and dichloroethane was also obtained as a by-product.

The reaction of formation of chlorofluoroethane can be expressed by the following equation:



By using the same method 1-bromo-2-fluoroethane, although in a considerably lower yield (up to 35%), was obtained from 2-bromoethyl ester of benzenesulfonic acid and potassium fluoride.

1-Chloro-2-fluoroethane $\text{CH}_2\text{ClCH}_2\text{F}$ is a mobile liquid with an odor resembling that of dichloroethane. It boils at $52-53^\circ\text{C}$ at normal pressure. Density d_4^{20} 1.1747 and d_4^{25} 1.2055; index of refraction n_D^{20} 1.3775. Freezing point below 50°C .

Chlorofluoroethane is miscible with most organic solvents and sparingly soluble in water. At room temperature 1 l. of water dissolves about 25 g. of 1-chloro-2-fluoroethane. 1-chloro-2-fluoroethane undergoes hydrolysis with difficulty; thus, by boiling with 7% sodium hydroxide solution for 2 hours, only 2% of chlorine ionized, and after 19 hours, 32%.

EXPERIMENTAL

Preparation of 1-chloro-2-fluoroethane from 2-chloroethyl ester of benzenesulfonic acid and aqueous potassium fluoride.

In a stainless steel autoclave were introduced the 2-chloroethyl ester of benzene sulfonic acid and 47-49% aqueous potassium fluoride in a ratio of 1.15 moles KF per mole of ester.

The mixture was stirred at a temperature of 150°C and the reaction products were gradually discharged through the cooled condenser at such a rate as to maintain the pressure in the autoclave at 2-3 atmospheres. Duration of reaction about 6 hours. The liquid in the receiver separated into two layers. The top layer represented water with traces of hydrofluoric acid, and the bottom layer was 1-chloro-2-fluoroethane, containing about 20% of 1,2-dichloroethane and up to 1.5% of vinyl chloride. 1-chloro-2-fluoroethane was isolated by distillation. Yield about 60% of theoretical.

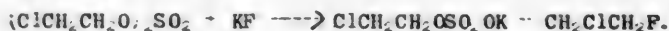
4.695 mg. substance:	5.080 mg. CO_2 ;	2.195 mg. H_2O
14.700 mg. substance:	8.838 ml. 0.02 N. AgNO_3 .	
2.2097 g. substance:	24.61 ml. 0.1 N. AgNO_3 .	
Found %:	C 29.51; H 5.20; Cl 42.64; F 22.29.	
Calculated %:	C 29.09; H 4.84; Cl 43.03; F 23.04.	

Preparation of 1-chloro-2-fluoroethane from 2-chloroethyl ester of benzene sulfonic acid and anhydrous potassium fluoride.

1 mole 2-chloroethyl ester of benzenesulfonic acid was heated with 1 mole of powdered potassium fluoride at 190°C . The volatile reaction products were distilled off and collected in a receiver. Fractionation yielded 1-chloro-2-fluoroethane, and as a by-product 1,2-dichloroethane. Yield of 1-chloro-2-fluoroethane was about 35% of theoretical.

Preparation of 1-chloro-2-fluoroethane from 2,2'-dichloro-diethylsulfate and potassium fluoride.

The initial 2,2'-dichlorodiethylsulfate was prepared by the method described by V.V. Nekrasov and Ya.F. Komissarov [1]. 1 mole of 2,2'-dichlorodiethylsulfate was mixed with 2 moles of finely powdered anhydrous potassium fluoride, and the mixture heated on an oil bath at 175°C ; 1-chloro-2-fluoroethane was distilled off and collected in a receiver. Yield of 1-chloro-2-fluoroethane was about 60% of theoretical, only one chloroethyl group being used. The reaction proceeded only to the formation of the potassium salt of 2-chloroethylsulfuric acid, according to the equation



Preparation of 1-bromo-2-fluoroethane

2-Bromoethyl ether of benzenesulfuric acid was treated in an autoclave with concentrated aqueous potassium fluoride under conditions given above in the description of the preparation of 1-chloro-2-fluoroethane. The reaction product, 1-chloro-2-fluoroethane, boiled at $71-72^\circ\text{C}$ (Henne and Renoll, [2] reported a b.p. $71.5-71.8^\circ\text{C}$). Yield of 1-bromo-2-fluoroethane was about 35% of theoretical. A large amount of 1,2-dibromoethane was obtained as a by-product.

*Fluoride was determined by Stark-Howley's method.

CONCLUSIONS

Methods of preparation of 1-chloro-2-fluoroethane and 1-bromo-2-fluoroethane have been discovered.

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THE REACTION OF ALIPHATIC OXIDES WITH HYDROGEN FLUORIDE I.

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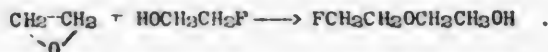
Aliphatic three-membered oxides may be readily split by substances containing active hydrogen atoms. Fission agents that can rupture the oxide ring possess hydrogen atoms varying widely in their activity. It appears surprising, therefore, that attempts to split ethylene oxide using hydrogen fluoride were unsuccessful.

Swarts [1], in a study of the action of hydrofluoric acid on ethylene oxide, showed that 30% hydrofluoric acid hydrates ethylene oxide to ethylene glycol; a small amount of polyethylene glycol is also formed. Epichlorohydrin under similar conditions forms glycerine monochlorohydrin, diglycerine chlorohydrin and high-boiling chlorinated compounds, not further identified. Swarts concluded that the oxides could not be split in this manner to yield the corresponding fluorohydrins.

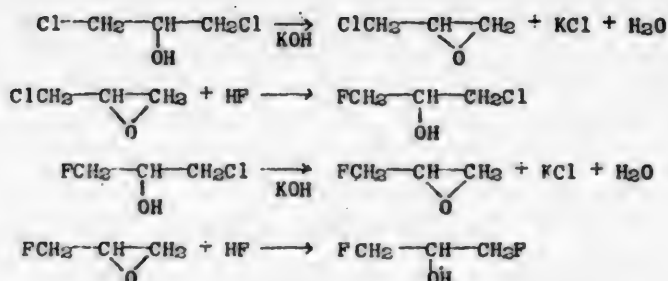
In our study, ethylene oxide reacting with anhydrous hydrogen fluoride under various conditions resulted in a chain polymerization of ethylene oxide. These chains were ruptured either by water present during the reaction or by hydrogen fluoride. The products obtained were polyethylene glycols and polyethylene fluorohydrins, and a very small amount of fluorine. The desired reaction product, ethylene fluorohydrin, occurs, if at all, in but very insignificant amounts. Attempts to reduce the polymerizing action of hydrogen fluoride by using its etherate or by attempting to maintain hydrogen fluoride in a monomeric state were unsuccessful. Desired results were obtained by reacting ethylene oxide with hydrogen fluoride in a dilute solution of ether. This dilution reduces the number of collisions of the oxide molecules. Polymerization is thus minimized and the predominating reaction becomes the formation of ethylene fluorohydrin.

Heating the 5% ether solution of ethylene oxide with an excess of hydrogen fluoride results in a 40% theoretical yield of ethylene fluorohydrin. The yield of ethylene fluorohydrin depends upon the concentration of ethylene oxide in the ether solution. Thus, ethylene fluorohydrin is obtained in 4 - 5% yield by the action of hydrogen fluoride on a 20% solution of the oxide; the highest yields are obtained at a 5 - 6% concentration of the oxide in the ether.

This investigation has shown that in addition to the formation of ethylene fluorohydrin, the β -fluoroethyl ether of glycol is also found in a 5 - 10% yield of theoretical, calculated on the basis of ethylene oxide. The structure of this compound was confirmed by converting it to β, β' fluorochlorodiethyl ether by reacting ethylene oxide with ethylene fluorohydrin:



Some other reaction products obtained were polyethylenefluorohydrin, a considerable amount of alcohol, and the monoethyl ether of glycol (up to 10% yield). Inasmuch as Calcott



High yields and the simple technique involved suggest a possible wide application of this new method of preparation of various fluoro organic substances not readily prepared using previous methods.

EXPERIMENTAL

1) 1 Fluoroethanol-2. Into a steel vessel capable of withstanding high pressures, 500 ml. of ether was introduced. The ether was cooled and 20 g. of anhydrous hydrogen fluoride and 20 g. of impurity-free dry ethylene oxide were carefully introduced. The vessel was sealed tightly and heated on a boiling water bath for six hours. The reaction mixture was then cooled and neutralized (congo red) with calcined soda. The neutral solution was decanted into a distilling flask provided with a long refluxing column. The ether was removed by distillation, the residue dried over anhydrous potassium fluoride and fractionated. Starting with 190 g. of ethylene oxide, the following fractions were collected: 78-80°, 3.2 g.; 98-105°, 122.5 g.; 132-135°, 37 g.; 172-174°, 21 g.; high boiling residue, 48 g.

The fraction of b.p. 98-105° represents pure ethylene-fluorohydrin. A repeated distillation yields a product of b.p. 102-104° (yield: 40% of theoretical).

Ethylenefluorohydrin is a clear mobile liquid with a mild pleasant odor.

B.P. 102-104°; d_{20}^{20} 1.102; n_D^{20} 1.364.

Found MR_D 12.98. Calculated MR_D 12.83

α -naphthyluretan -- colorless needles (from ligroin) m.p. 125-127°.

Found %: N 6.27

$C_2H_2O_2NF$. Calculated %: N 6.00

Fraction b.p. 132-135°, monoethyl ether of glycol -- transparent colorless mobile liquid.

d_{20}^{20} 0.9588; n_D^{20} 1.4085; found MR_D 23.74, calculated MR_D 23.37.

Found %: C 52.80; H 10.90

$C_4H_{10}O_2$. Calculated % C 52.30 H 11.00

Fraction b.p. 172-174°, β -fluoroethyl ether glycol -- colorless liquid with a pleasant odor.

d_{20}^{20} 1.1150; n_D^{20} 1.4130; found MR_D 24.17; calculated MR_D 23.74.

Found %: C 44.1; H 8.38

$C_4H_8O_2F$. Calculated % C 44.40; H 8.33

All subsequent experiments in splitting three-member oxides with anhydrous hydrogen fluoride were conducted under conditions similar to those described in the preparation of ethylene fluorohydrin.

Therefore the details of the following experiments will be omitted.

2) 1-Fluoropropanol-2 Ether 500 ml., anhydrous HF 10 g., propylene oxide 25 g. Duration of heating: 4 hours. After removal of ether, the residue was dried over anhydrous KF and fractionated. The fractionation yielded isopropylenefluorohydrin, a clear liquid with a mild pleasant odor.

b.p. 107-108°; Yield 56% of theoretical.

d_{20}^{20} 1.0214; n_D^{20} 1.3822 found MR_D 17.77; calculated MR_D 17.47.

Found %: F 24.32

C_3H_7OF . Calculated %: F 24.39

α -naphthylurethane -- a crystalline powder (from ethylacetate); b.p. 81-83°.

Found %: N 5.90

$C_{14}H_{14}O_2NF$. Calculated %: N 5.66.

3) 1,3-Difluoropropanol-2. Ether 500 ml., anhydrous HF 10 g., epifluorohydrin 20 g. Duration of heating: 6 hours. After removal of ether, the residue was dried over anhydrous KF and fractionated under reduced pressure. 1,3-difluoropropanol-2 -- a clear mobile liquid with a slight odor.

b.p. 59° at 40 mm.; Yield 40% of theoretical.

d_{20}^{20} 1.2443; n_D^{20} 1.380; found MR_D 17.96; calculated MR_D 17.37.

Found %: C 37.11; H 6.60

$C_3H_5OF_2$. Calculated %: C 37.50 H 6.25.

4) 1-Fluoro-2-methylpropanol-2. Ether 200 ml., anhydrous HF 11.0 g., isobutylene oxide 20 g. Duration of heating: 2 hours. The excess of HF was combined with moist KF. The ether was distilled off and the residue distilled under reduced pressure. Fraction of a boiling point 50-51° at 63 mm. was treated with water; the water insoluble oil was separated and dried over KF. The b.p. of tetramethyldioxane under atmospheric pressure 136-137°.

d_{20}^{20} 0.8906; n_D^{20} 1.4130; found MR_D 40.42; calculated MR_D 40.23.

From the aqueous solution isobutylenefluorohydrin was extracted with ether after salting out with NaCl. The ether extract was dried over anhydrous KF, the ether distilled off, and the residue distilled under reduced pressure. B.p. of isobutylenefluorohydrin 58° at 82 mm.

d_{20}^{20} 0.9610; n_D^{20} 1.3913; found MR_D 22.7; calculated MR_D 22.09.

Found %: F 18.05

C_4H_9OF . Calculated %: F 20.65

5) Epifluorohydrin. Into a round bottom flask, provided with a stirrer, reflux condenser, thermometer and a wide short tube, were introduced 150 ml. of absolute ether, 40 g. 1,3-fluorochloropropanol-2, and with cooling and continuous stirring, powdered potassium hydroxide over a period of 15-20 minutes. The contents of the flask were maintained at boiling with continuous stirring for 3 hours.

The ether solution of epifluorohydrin was decanted and the residue washed three times with small portions of dry ether. The ether extract was added to the main solution. The ether was removed by distillation, the residue dried over anhydrous KF and fractionated. After repeated distillation, the boiling point of epifluorohydrin 85-86.4°. Yield 75% of theoretical. Epifluorohydrin -- a clear mobile liquid with a faint ethereal odor.

d_{20}^{20} 1.090; n_D^{20} 1.373; found MR_D 15.89; calculated MR_D 15.94.

Found %: C 46.93; H 7.08

C_3H_5OF . Calculated %: C 47.37; H 6.58.

6) 1,3-Fluorochloropropanone. Into a round bottom flask provided with a stirrer, thermometer and dropping funnel, were introduced a solution of sodium dichromate (75 g. $\text{Na}_2\text{Cr}_2\text{O}_7$ + 43 ml. H_2O), 1,3-chlorofluoropropanol-2 50 g., and, with continuous stirring and cooling over a period of 3 hours, H_2SO_4 (90 g. concentrated H_2SO_4 + 23 ml. H_2O). The stirring was continued for 15-17 hours. The oxidation products were repeatedly extracted with benzene. The benzene solution was washed with water until neutral, and dried over freshly ignited magnesium sulfate. The benzene was removed by distillation and the residue fractionated, first under reduced pressure and then at atmospheric. 1,3-Fluorochloropropanone — colorless clear liquid, lachrymatory in nature.

b.p. 141.5-143.5° at 760 mm.; d_{20}^{20} 1.296; n_D^{20} 1.4235; found M_R 21.7; calculated M_R 20.9.

Found %: Cl 32.20
 $\text{C}_3\text{H}_4\text{OFCI}$. Calculated %: Cl 32.13

Semicarbazone crystals (from alcohol) m.p. 111-112°.

Found %: N 25.54
 $\text{C}_4\text{H}_7\text{OFCIN}_3$. Calculated %: N 25.07.

7) β -Fluoroethyl ether of glycol. Into a pressure-resistant steel vessel were introduced: ethylenefluorohydrin 40 g (3 moles) and with cooling, ethylene oxide 10 g. The tightly closed vessel was heated to a temperature of 170-180° over a period of 54 hours. After distilling off ethylene fluorohydrin (32.4 g.) the residue was fractionated. β -Fluoroethylether of glycol. A glycerine-like liquid with a fruity odor.

B.p. 172-174°; d_{20}^{20} 1.1144; n_D^{20} 1.4130; found M_R 24.17; calculated M_R 23.77.

Found %: C 44.09; H 8.38.
 $\text{C}_4\text{H}_6\text{O}_2\text{F}$. Calculated %: C 44.40; H 8.13.

CONCLUSIONS

1) Aliphatic three-membered oxides can be made to react readily with anhydrous hydrogen fluoride with the formation of fluorohydrin glycols.

2) Heating dilute ether solutions of the corresponding oxides with anhydrous hydrogen fluoride gives good yields of: ethylenefluorohydrin, propylenefluorohydrin, 1,3-difluoropropanol 2, isobutylenefluorohydrin, and others.

3, It has been shown that the order of addition of hydrogen fluoride to ethylene oxide is similar to the addition of the other hydrogen halides.

4) This new method of formation of a fluorocarbon bond now makes readily available many fluorine derivatives of aliphatic compounds.

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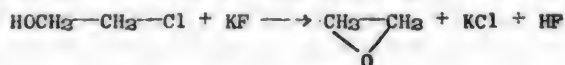
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THE REACTION OF ALIPHATIC OXIDES WITH HYDROGEN FLUORIDE. II.

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A new reaction for the splitting of aliphatic oxides by hydrogen fluoride was described in a preliminary communication. This resulted in the formation of glycol fluorohydrins. Another method of preparing glycol fluorohydrins and, in particular, ethylenefluorohydrin, could be by a direct replacement of chlorine atoms in ethylenechlorohydrin by fluorine. This reaction, as shown experimentally, proceeds in two stages, and finally consists in the interaction of ethylene oxide with potassium bifluoride. The ethylene oxide was first formed from the ethylenefluorohydrin under the action of potassium fluoride. Anhydrous ethylenechlorohydrin when boiled with anhydrous potassium fluoride splits off hydrogen chloride and gives a quantitative yield of ethylene oxide. Hydrogen chloride, by a metathetic reaction with potassium fluoride, yields potassium chloride and hydrogen fluoride. The latter with potassium fluoride forms bifluoride:



Thus, potassium fluoride functions as a primary alkali. In a similar manner, glycerine monochlorohydrin yields glycidic alcohol, and glycerine difluorohydrin yields epichlorohydrin. The "alkaline" properties of potassium fluoride are so pronounced that, by using it, it is possible to split off hydrogen chloride from the halogen compounds with the formation of olefins; thus, bornyl chloride when heated with anhydrous potassium fluoride gives an almost quantitative yield of camphenes.

When the reaction of ethylenechlorohydrin with anhydrous potassium fluoride is conducted under pressure, or when ethylene oxide and bifluoride are heated in an autoclave, ethylenefluorohydrin is formed in a 35-40% yield of theoretical. Thus, the reaction of ethylenechlorohydrin with potassium fluoride proceeds in two stages: first ethylene oxide is formed, which subsequently is split by bifluoride with the formation of ethylenefluorohydrin.

The high yields obtained and the simplicity of the procedures suggest a wide application for this new method of preparing various fluoro-organic compounds, not obtainable by earlier methods. Thus compounds with different functional groups could only rarely be obtained from the corresponding chloro and bromo derivatives by metathetic reactions.

In the first article, a description was given of a series of reactions and derivatives of fluorine containing alcohols, chlorofluoroacetone, epifluorohydrin, and others. In subsequent conversions, fluoroacetals, fluorine substituted acids, fluorinated ethers and esters, fluorine substituted esters of mineral acids, fluoroalkylamines, fluorinated hydrocarbons, etc., were obtained. The types and properties of the obtained fluorides are tabulated herein.

Among the derivatives of fluorohydrins, the esters of the latter occupy a special place; they are obtained readily by the action of halogen anhydrides of organic and inorganic acids on fluorohydrins: tri β fluoroethylphosphite, tri β fluoroethylphosphate, bis β fluoroethylsulfate, β fluoroethylchlorosulfate, β fluoroethylchlorocarbonate, di β fluoroethylcarbonate, β fluoroethylnitrate, β fluoroethyl *n* tolylsulfonate, β fluoroethylbenzenesulfonate and others.

A number of these esters of sulfonic acids have a strong alkylating action. In using them, because of a comparative stability of the fluoro-carbon bond, the β fluoro-ethylation of a series of compounds was obtained. Thus, by using β fluoroethyl esters of sulfonic acids we obtained: β fluorophenetol from phenol, 1,2-fluoroiodoethane from potassium iodide, β fluorotriethylamine from diethylamine, β fluoroethylbenzene from phenyl magnesium bromide, and others. Thus, fluorinated derivatives (in α - and β - positions) of various classes of organic substances became available. By means of these reactions, it is possible to synthesize compounds with several functional groups without disturbing the fluorine bond. Such reaction products are obtained only with great difficulty by other methods. Under somewhat more severe conditions, fluorine atoms in these compounds can be protected by conversions characteristically used with the other halogen derivatives. Thus, the possibilities of synthesis are of wide scope.

EXPERIMENTAL PART

1) Ethylfluorohydrin and potassium fluoride. Into a round bottom flask provided with a refluxing column connected with a trap, 80.5 g. of pure ethylenechlorohydrin and 118 g. of anhydrous potassium fluoride were added with cooling. The mixture was refluxed on an oil bath. The formation of ethylene oxide started at once, condensing in the trap. The yield of ethylene oxide was 40 g., representing 90% of the theoretical yield. The residue in the flask consisted of an equimolecular mixture of potassium chloride and bifluoride.

2) Ethylenefluorohydrin. In a steel vessel of 0.75 liter capacity were introduced 118 g. potassium trifluoride and 81 g. ethylenechlorohydrin. The vessel was heated on an oil bath at a temperature of 100-110° for 4-5 hours. After cooling, the reaction mixture was extracted with ether. The ether extract was dried with potassium fluoride and distilled through a column containing Fenske rings. After three fractionations, there was obtained 19.5 g. of pure ethylenefluorohydrin, b.p. 101-103°; yield 30% of theoretical.

3) α -chloromethyl β -fluoroethyl ether. In a flask provided with a reflux condenser and tube for passing HCl, 19.2 g. (0.3 moles) ethylenefluorohydrin, 49.0 g. (0.1 mole) trihydroxymethylene were added. The reaction mixture was cooled with ice and saturated with dry hydrogen chloride gas until the trihydroxymethylene was completely dissolved. After standing for 24 hours at room temperature, the liquid separated into two layers. The upper aqueous layer was removed. The lower layer was dried over freshly ignited magnesium sulfate; hydrogen chloride was removed by passing a current of dry nitrogen for 6 hours, and then doubly distilling the residue in an atmosphere of nitrogen. α chloromethyl β fluoroethyl ether - a colorless mobile liquid with a slight odor of formalin; yield 60% of theoretical.

B.p. 42-43° at 60 mm.

d_{20}^{20} 1.190; n_D^{20} 1.4120; M_D 23.50; % Cl 30.54

C_2H_5OFCI . Calculated M_D 22.46; % Cl 31.5

4) β, β' -Chlorofluorodiethyl ether. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 20 g. β fluoroethyl ether of glycol and 30 ml. absolute benzene, 14.4 g. dry pyridine and gradually, with cooling and con-

tinuous shaking, 21.4 g. thionyl chloride. After complete addition of the thionyl chloride, the reaction mixture was heated on a boiling water bath until no further evolution of SO_2 . After cooling, pyridine hydrochloride precipitated, was filtered off and washed with small portions of dry benzene; the extracts were added to the filtrate and neutralized with dry soda. Benzene was distilled off and the residue fractionated. After repeated distillation, 8.4 g. β, β' -chlorofluorodiethyl ether was isolated. Yield 24% of theoretical; clear liquid:

B.p. 142-147° d_{20}^{20} 1.137;

n_D^{20} 1.4170; M_D 28.00; % Cl 27.60

$\text{C}_4\text{H}_8\text{OFCI}$. Calculated M_D 27.79; % Cl 28.03.

5) β -Fluorophenetole. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 30 ml. methyl alcohol and 1.15 g. metallic sodium (0.05 moles). The methylate was cooled, mixed with 4.7 g. pure phenol (0.05 moles), and while being thoroughly shaken, with 11 g. (0.05 moles) β -fluoroethyl ester of p-toluenesulfonic acid. After 20 minutes, sodium p-toluene sulfonate precipitated. To complete the reaction, the mixture was heated on a water bath for 4 hours. Methyl alcohol was distilled off, the residue treated with water, and fluorophenetole extracted with ether. The ether solution was washed repeatedly with 30% NaOH solution, then with water and dried over freshly ignited potassium fluoride. The ether was distilled off, and the residue distilled under vacuum. 4 g. of β -fluorophenetole separated. This appeared as colorless plate-like crystals, m.p. 36.5° and b.p. 88-90° at 16 mm.

Found %: C 68.0; H. 6.68

$\text{C}_8\text{H}_9\text{OF}$. Calculated %: C 68.57; H 6.42.

6) β, β' -Difluorodiethyl ether of methylene glycol (β, β' -difluoroethylal). Into a flask, provided with a reflux condenser and tube for passing hydrogen chloride, were introduced 30.0 g. (0.47 moles) ethylenefluorohydrin and 4.5 g. (0.05 moles) trioxymethylene. After cooling with ice, the reaction mixture was saturated with dry hydrogen chloride until the trioxymethylene dissolved completely. After standing for 72 hours at room temperature the liquid was carefully neutralized with solid, slightly moistened soda. The oil which separated after neutralization was dried with freshly ignited potassium fluoride and distilled under atmospheric pressure.

β, β' -Difluorodiethyl ether of methylene glycol - clear oily liquid with a pleasant ethereal odor; b.p. 162-164°; yield 50% of theoretical.

d_{20}^{20} 1.1302; n_D^{20} 1.3860; M_D 29.05.

$\text{C}_5\text{H}_{10}\text{O}_2\text{F}_2$. Calculated: M_D 28.47.

Found %: C 42.72; H 7.25

$\text{C}_5\text{H}_{10}\text{O}_2\text{F}_2$. Calculated %: C 42.85; H 7.14.

7) β, β' -Difluorodiethylacetal. Into a flask, provided with a reflux condenser and dropping funnel were introduced 40 g. (0.62 moles) ethylenefluorohydrin, 15.9 g. (0.1 moles) freshly ignited blue vitriol. 14.2 g. (0.32 moles) of freshly distilled acetaldehyde was then added slowly with continuous shaking, while cooling the mixture with ice. The reaction mixture was allowed to stand at room temperature for 10 days. The blue vitriol, which turned to green, was filtered off, and the filtrate fractionated. β, β' -Difluorodiethylacetal - colorless liquid with a sharp odor. b.p. 80° at 30 mm.; Yield 20% of theoretical.

d_{20}^{20} 1.0914; n_D^{20} 1.3936; M_D 33.57.

$\text{C}_6\text{H}_{12}\text{O}_2\text{F}_2$. Calculated: M_D 33.068.

Found %: C 46.15; H 7.79

$\text{C}_6\text{H}_{12}\text{O}_2\text{F}_2$. Calculated %: C 46.75; H 7.79.

8) β -Fluoroethylnitrite. Into a round bottom flask, fitted with a thermometer, reflux condenser and dropping funnel, were introduced 20 g. ethylenefluorohydrin and a saturated aqueous solution of sodium nitrite (22 g. NaNO_2 + 40 ml. H_2O). The solution was cooled to -5° , and at a temperature between 0° to -5° , 25 ml. of concentrated hydrochloric acid (d 1.19) was then added slowly with thorough shaking. The upper layer was separated, rapidly washed successively with ice-water, a dilute solution of soda, then again with water; dried over freshly prepared potassium fluoride and distilled at atmospheric pressure. There was obtained 11.4 g β fluoroethylnitrite with b.p. (after repeated distillation, $65-66^\circ$; yield 40%. Colorless mobile liquid with a pleasant almond-like odor; decomposes when stored in air.

d_{20}^{20} 1.1409; n_D^{20} 1.3572; MR_D 17.80.
 $\text{C}_2\text{H}_4\text{O}_2\text{NF}$. Calculated: MR_D 17.19.

9) Tri- β -Fluoroethylphosphite (in collaboration with N.M. Korneichuk). Into a round bottom flask, provided with a stirrer, reflux condenser, thermometer and dropping funnel, were introduced 32 g. (3 moles) pyridine and 50 ml. absolute ether. To the mixture, with continuous stirring, a solution of 22.9 g. (1 mole) of phosphorous trichloride and 20 ml. absolute ether was added. The reaction temperature ($5-6^\circ$) was controlled by the rate of addition of phosphorous trichloride; time of addition was 3 hours. Upon completion of addition, the stirring was continued at room temperature for another 2 hours. The precipitated pyridine hydrochloride was filtered off rapidly, washed several times with small portions of absolute ether and dried in a vacuum desiccator. The ether was distilled off from the combined ether extracts, and the residue repeatedly fractionated under reduced pressure.

Tri- β -fluoroethylphosphite boils at a temperature of $114-116^\circ$ at 8 mm.; colorless, mobile liquid with an unpleasant odor resembling hydrogen phosphite; this compound has a depressant effect on the central nervous system.

d_{20}^{20} 1.285; n_D^{20} 1.417; MR_D 43.08; % F 24.24.
 $\text{C}_6\text{H}_{12}\text{O}_3\text{F}_3\text{P}$ Calculated: MR_D 42.74 % F 25.90.

10) β -Fluoroethyl ester of dichlorophosphoric acid. Into a round bottom flask, provided with a stirrer, dropping funnel, thermometer and reflux condenser, were introduced 54 g. of phosphorous oxychloride. To this, 23 g. of ethylenefluorohydrin were added with thorough stirring and cooling with cold water. The temperature of the reaction ($20-22^\circ$) was controlled by the rate of addition of ethylenefluorohydrin. Upon completion of addition, the stirring was continued at room temperature for another 5 hours. Hydrogen chloride was removed by passing through a stream of dry CO_2 . The reaction products were fractionated under reduced pressure. Fraction of b.p. $106-107^\circ$ at 30 mm represents β -fluoroethyl ester of dichlorophosphoric acid; yield 20.5 g. or 35.4% of theoretical.

d_{20}^{20} 1.5367; n_D^{20} 1.4400; MR_D 30.70; % Cl 40.33
 $\text{C}_2\text{H}_4\text{O}_2\text{PFCl}_2$. Calculated. MR_D 30.54; % Cl 39.20.

11) Tri β -fluoroethylphosphate. Into a round bottom flask, provided with a stirrer, thermometer, reflux condenser and dropping funnel, were introduced 29.0 g. (3 moles) ethylene fluorohydrin, 39.3 g. (3 moles) pyridine and 40 ml. absolute benzene. To the mixture, with continuous stirring, was gradually added a solution of 23.2 g. (1 mole) phosphorous oxychloride and 20 ml. benzene. The reaction temperature (not above 30°) was controlled by the rate of addition of phosphorous oxychloride. Pyridine hydrochloride was precipitated. Upon completion of addition of POCl_3 , the temperature was raised to

55°, and stirring continued at this temperature for another hour. The reaction mixture was cooled, the precipitated pyridine hydrochloride filtered off rapidly, and washed several times with small portions of absolute ether. The ether extracts were added to the benzene solution. The solvents were distilled off and the residue fractionated under reduced pressure. After repeated distillation, the boiling point of tri-β-fluoroethyl-phosphate was 169° at 11 mm; yield 60% of theoretical. Colorless oily liquid with a mild pleasant odor of ether.

d_{20}^{20} 1.365; n_D^{20} 1.4043; MR_D 42.00; % P 23.38

$C_8H_{12}O_4F_3P$. Calculated MR_D 42.48; % P 24.15.

12) β-Fluoroethylchlorosulfonate. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 25.0 g. sulfuryl chloride and gradually, with shaking, 6.4 g. ethylene fluorohydrin. Initially, the temperature was maintained at 35-40°; toward the completion of the reaction, after evolution of hydrogen chloride had stopped, the temperature was raised to 60°. Hydrogen chloride was removed by passing a current of dry air through, and the condensation product was distilled under vacuum. One fraction was separated with a b.p. 79-80° at 18 mm. -- 16.21 g.; another fraction of b.p. 81-82° at 2 mm. -- 4.3 g. The first fraction is β-fluoroethylchlorosulfonate. Colorless mobile liquid with a sharp unpleasant lachrymatory odor; yield 62% of theoretical.

d_{20}^{20} 1.4970; n_D^{20} 1.4198; MR_D 27.460.

Calculated: MR_D 27.79.

The fraction with b.p. 81-82° at 2 mm. represents β,β'-dichlorodiethyl sulfate; yield 12% of theoretical.

13, β,β'-Difluorodiethyl sulfate. Into a round bottom flask, provided with a reflux condenser and dropping funnel were introduced 12.8 g. ethylene fluorohydrin and, with shaking and cooling an equimolar amount of sulfuryl chloride. Upon completion of addition, the reaction mixture was heated on a water bath at a temperature of 60-70° for 24 hours. Hydrogen chloride was removed by passing a current of dry air through, and the reaction product was distilled under vacuum. Colorless mobile liquid with a mild, pleasant ether odor.

b.p. 82-84° at 2 mm.

d_{20}^{20} 1.3191; n_D^{20} 1.4080;

MR_D 35.65; % C 25.01; % H 4.87

$C_4H_8O_4SF_2$. Calculated % C 25.25; % H 4.22.

14, β-Fluoroethyl ester of p-toluenesulfonic acid. Into a round bottom flask, provided with a stirrer, dropping funnel and thermometer, were introduced 3 moles of ethylene fluorohydrin, 1 mole p-toluenesulfochloride. With cooling and continuous stirring at a temperature of 6-10° a 30% sodium hydroxide solution was slowly added until the mixture was alkaline to phenolphthalein; the stirring of the reaction mixture was continued for another 5-8 hours. The precipitated NaCl was filtered off. The lower layer was separated, washed with water, dried under vacuum and distilled under reduced pressure. The upper layer consisting of excess ethylene fluorohydrin was used for the subsequent experiment. Yield of ester: 85-95% of theoretical.

b.p. 174-175° at 10 mm. % C 48.90; % H 5.20

$C_9H_{10}O_3FS$. Calculated % C 49.08; % H 5.08

15, β-Fluorotriethanolamine. Into a combustion tube were introduced 20 g. β-fluoroethyl ether of p-toluenesulfonic acid and 7.7 g. diethylamine. The tube was sealed

and heated on a boiling water bath for 3 hours; upon cooling, the contents of the tube crystallized. The reaction mixture was dissolved in 15 ml. water, salted out with sodium hydroxide and extracted with ether. The ether extract was dried over fused KOH, the ether was distilled off, and the residue then distilled at atmospheric pressure.

B.p. 107-113°; d_{20}^{20} 0.8775; n_D^{20} 1.400; MR_D 33.64.

C_8H_7NF . Calculated: MR_D 33.74.

Picrate of β fluorotriethylamine - light yellow crystals (from alcohol) of a m.p. 134-136°.

16) β -Fluoroethylbenzene. In a flask, fitted with a reflux condenser and dropping funnel, an ether solution of phenyl magnesium bromide (15.7 g. bromobenzene, 2.4 g. magnesium and 40 g. absolute ether) was prepared. To this, with thorough shaking, was gradually added the ether solution of β fluoroethyl ether of p-toluenesulfonic acid (21.9 g. and 60 ml. absolute ether). The reaction was exothermic, the ether boiling. A white voluminous precipitate separated out. On the following day, the reaction mixture was heated on a water bath for 3 hours; then it was cooled, and the contents of the flask treated slowly with dilute sulfuric acid until the precipitate was completely dissolved.

The reaction product was repeatedly extracted with ether. The ether extract was washed with a soda solution and then with water until neutral, and then dried over freshly ignited potassium fluoride. The ether was distilled off, and the residue distilled under reduced pressure. The main fraction boiled at a temperature of 57-60° at 14 mm. Boiling point at atmospheric pressure 157-160°; yield 30% of theoretical. Colorless mobile liquid with a mild pleasant odor.

d_{20}^{20} 1.064 n_D^{20} 1.4965; MR_D 34.05; $\%F$ 12.7.

C_8H_9F . Calculated: MR_D 35.44; $\%F$ 15.3.

17) β -Fluoroethylchlorocarbonate. In a flask provided with a stirrer, dropping funnel, and reflux condenser were condensed 90 g. phosgene, and, with cooling and continuous stirring, 20 g. of ethylenefluorohydrin were slowly added. The rate of addition was governed by the desired temperature (-5 to 0°). Upon completion of addition of ethylene fluorohydrin, the reaction mixture was allowed to stand for 48 hours at a temperature of 0 to 2°. The excess of phosgene was removed by passing a current of dry air through. The residue, a heavy oil with a light orange color, was distilled under atmospheric pressure. B. p. β -fluoroethylchlorocarbonate 129-131°; yield 81% of theoretical; colorless liquid with sharp lachrymatory properties.

d_{20}^{20} 1.362; n_D^{20} 1.4020 MR_D 22.61.

$C_2H_4O_2ClF$. Calculated: MR_D 22.58.

18) β, β' -Difluorodiethylcarbonate. Into a round bottom flask, provided with a reflux condenser, were introduced 3.2 g. ethylenefluorohydrin and 6.3 g. β -fluoroethylchlorocarbonate. The reaction was carried out at a temperature of 140-160° for 24 hours. Upon completion of heating, the reaction mixture was distilled under vacuum. After repeated distillation there was separated β, β' -difluorodiethylcarbonate. B.p. 95-98° at 16 mm.; Yield 45% of theoretical. Colorless liquid with a pleasant odor.

d_{20}^{20} 1.2552; n_D^{20} 1.3940; MR_D 29.34.

$C_4H_8O_3F_2$. Calculated: MR_D 28.53.

19) Fluoroacetic acid. In a three-neck flask, provided with a stirrer and dropping funnel, was introduced an aqueous solution of ethylenefluorohydrin (15 g. ethylenefluorohydrin + 50 ml. water). To this $KMnO_4$ (about 20 g.), and a 10% solution of NaOH.

(30 ml. 10% NaOH per 15 g. ethylenefluorohydrin) were added together. The addition was gradual, a fresh portion of permanganate being added after each discoloration. Upon completion of oxidation, manganese dioxide was filtered off. The filtrate was neutralized with dilute H_2SO_4 and evaporated under vacuum. The dry residue of sodium fluoroacetate was decomposed by distilling with concentrated sulfuric acid. The distillate, aqueous fluoracetic acid, was dried over Na_2SO_4 , then $CuSO_4$, and then redistilled. B.p. 159-163°. The oxidation is very slow, requiring several days; the yield of acid is less than 10% of theoretical. In the decomposition of the dry residue, strong foaming accompanied by an evolution of hydrogen fluoride was observed.

20, Chloroanhydride of fluoroacetic acid. Into a wide tube closed at one end and connected with a Liebig condenser, were introduced completely dried sodium fluoroacetate and phosphorus pentachloride (1 mole PCl_5 per 3 moles of sodium fluoroacetate). Upon heating the reaction mixture on an oil bath at a temperature of 140-150° the chloroanhydride of the fluoroacetic acid was distilled off. After repeated distillation, b.p. 72-75°. Chloroanhydride -- clear, colorless liquid with strong lachrymatory properties. The compound fumes when exposed to air. Yield 35% of theoretical.

$$d_{20}^{20} 1.3813; n_D^{20} 1.409; \% Cl 36.52.$$

$$C_2H_2OFCl. \text{ Calculated: } \% Cl 36.78.$$

21) β -Fluoroethylfluoroacetate. Into a flask provided with a reflux column and connected to a straight condenser, were introduced 34 g. of mercuric fluoride (previously mixed with 18 g. of freshly ignited potassium fluoride) and 29 g. β -fluoroethylfluoroacetate. The reaction mixture was gradually heated to 135° (on a bath) and then maintained at this temperature for 5 hours. Upon completion of heating, the apparatus was attached to a vacuum pump and β -fluoroethylfluoroacetate distilled off, at 20 mm. After repeated distillation, b.p. of β -fluoroethylfluoroacetate 78-80° at 35 mm. yield 24.5% of theoretical. Colorless, slightly mobile liquid with a faint odor.

$$d_{20}^{20} 1.2862 \quad n_D^{20} 1.3900; MR_D 22.85.$$

$$C_4H_6O_2F_2 \text{ Calculated: } MR_D 22.23.$$

22) β -Fluoroethylchloroacetate. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 6.7 g. ethylenefluorohydrin and gradually, with shaking, 10.0 g. chloroacetylchloride. After addition of the chloroanhydride, the reaction mixture was heated on a boiling water bath until the evolution of hydrogen chloride ceased (3 hours). The remaining hydrogen chloride was removed by washing with small portions of iced water. The neutral solution was dried over freshly ignited potassium fluoride and distilled twice under vacuum. Yield 30% of theoretical. Colorless mobile liquid with strong lachrymatory properties.

$$B.p. 83-85^\circ \text{ at } 15 \text{ mm. } d_{20}^{20} 1.4065; n_D^{20} 1.3900; MR_D 27.30.$$

$$C_4H_6O_2ClF. \text{ Calculated: } MR_D 27.20.$$

23) β -Fluoroethylbromoacetate. In a round bottom flask, provided with a reflux condenser and a dropping funnel, were introduced 8 g. ethylenefluorohydrin and gradually, with shaking, 20 g. bromoacetyl bromide. The reaction mixture was heated on a boiling water bath until the evolution of hydrogen bromide ceased. The remaining hydrogen bromide was removed by washing with iced water until neutral. The neutral solution was dried over anhydrous potassium fluoride and distilled twice under vacuum.

β -Fluoroethylbromoacetate -- heavy slightly colored liquid with strong lachrymatory properties. B.p. 87-90° at 12 mm; decomposes at atmospheric pressure. Yield 50% of theoretical.

Table of Synthesized Fluorides

Formula	boiling point °C	pres. mm	melting point °C	Spec. grav. at 20°	Index of re- frac- tion at 20°	Method of preparation
$\text{FCH}_2\text{---CH}_2\text{OH}$	102—104	760	--	1.102	1.3640	$\text{CH}_3\text{---CH}_2 + \text{HF: ClCH}_2\text{---CH}_2\text{OH} + \text{KF}$
$\alpha\text{-C}_{10}\text{H}_7\text{NH---C(=O)OCH}_2\text{CH}_2\text{F}$	--	--	125—126	--	--	$\text{FCH}_2\text{CH}_2\text{OH} + \alpha\text{-C}_{10}\text{H}_7\text{NCO}$
$\text{FCH}_2\text{CH(OH)---CH}_3$	107—108	760	--	1.021	1.3822	$\text{CH}_3\text{---CH---CH}_2 + \text{HF}$
$\alpha\text{-C}_{10}\text{H}_7\text{---C(=O)OCH(CH}_3\text{)CH}_3$	--	--	81—83	--	--	$\text{CH}_3\text{CH(OH)---CH}_2\text{F} + \alpha\text{-C}_{10}\text{H}_7\text{NCO}$
$\text{FCH}_2\text{---CH(OH)---CH}_2\text{Cl}$	153—156	760	--	1.300	1.4360	$\text{ClCH}_2\text{---CH---CH}_3 + \text{HF}$
$\text{FCH}_2\text{---CH(OH)---CH}_2\text{F}$	58—60	40	--	1.244	1.3820	$\text{FCH}_2\text{CH---CH}_3 + \text{HF}$
$\text{FCH}_2\text{---C(CH}_3\text{)(OH)---CH}_3$	58—59	82	--	0.9910	1.3913	$\text{CH}_3\text{---C(CH}_3\text{)---CH}_3 + \text{HF}$
$\text{FCH}_2\text{---CH---CH}_2$ 	85 86.5	760	--	1.090	1.3730	$\text{FCH}_2\text{CH(OH)---CH}_2\text{Cl} + \text{KOH}$
$\text{FCH}_2\text{---C(=O)---CH}_2\text{Cl}$	141.5—143.5	760	--	1.296	1.4235	$\text{FCH}_2\text{CH(OH)CH}_2\text{Cl} + \text{O}$
$\text{FCH}_2\text{---C(=O)---CH}_2\text{Cl}$ 	--	--	111—112	--	--	$\text{FCH}_2\text{---C(=O)---CH}_2\text{Cl} + \text{H}_2\text{N---NH---CO---NH}_2$
$\text{FCH}_2\text{CH}_2\text{---OCH}_2\text{---CH}_2\text{OH}$	172—174	760	--	1.114	1.4130	$\text{CH}_3\text{---CH}_2 + \text{FCH}_2\text{---CH}_2\text{OH}$
$\text{ClCH}_2\text{O---CH}_2\text{CH}_2\text{F}$	42—43	68	--	1.190	1.4120	$\text{CH}_2\text{F---CH}_2\text{OH} + (\text{CH}_2\text{O})_3 + \text{HCl}$
$\text{FCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$	142—147	760	--	1.137	1.4170	$\text{FCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{SOCl}_2$
 $\text{---O---CH}_2\text{CH}_2\text{F}$	88—90	16	36.5	--	--	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{CH}_2\text{F} + \text{C}_6\text{H}_5\text{OH}$
$\text{CH}_2\text{---OCH}_2\text{CH}_2\text{F}$ 	162—164	760	--	1.130	1.3860	$\text{FCH}_2\text{CH}_2\text{OH} + (\text{CH}_2\text{O})_3 + \text{HCl}$
$\text{CH}_3\text{---CH---OCH}_2\text{CH}_2\text{F}$ 	80 167—168	30	--	1.091	1.3936	$\text{FCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{---C(=O)---H} + \text{CuSO}_4$
$\text{FCH}_2\text{CH}_2\text{---O---N=O}$	65—66	760	--	1.141	1.3572	$\text{FCH}_2\text{CH}_2\text{OH} + \text{NaNO}_2 + \text{HCl}$
$\text{P(OCH}_2\text{CH}_2\text{F})_3$	114—116	8	--	1.285	1.4170	$\text{FCH}_2\text{CH}_2\text{OH} + \text{PCl}_3$
$\text{O---P(OCH}_2\text{CH}_2\text{F)(Cl)}$	106—107	30	--	1.537	1.4400	$\text{FCH}_2\text{CH}_2\text{OH} + \text{POCl}_3$
$\text{O---P(OCH}_2\text{CH}_2\text{F)}_3$	169	11	--	1.365	1.4043	$\text{FCH}_2\text{CH}_2\text{OH} + \text{POCl}_3$
$\text{SO}_2\text{---Cl}$ 	80	18	--	1.497	1.4298	$\text{FCH}_2\text{CH}_2\text{OH} + \text{SO}_2\text{Cl}_2$

Formula	boiling point °C	pres. mm.	melting point °C	Spec. grav. at 20°	Index of re- frac- tion at 20°	Method of preparation
$\text{SO}_2 \begin{array}{l} \diagup \text{OCH}_2\text{CH}_2\text{F} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	82—84	2	--	1.319	1.4080	$\text{FCH}_2\text{CH}_2\text{OH} + \text{SO}_2 \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$
$\text{CH}_3 \text{---} \text{C}_6\text{H}_4 \text{---} \text{SO}_2\text{O} \text{---} \text{CH}_2\text{CH}_2\text{F}$	174—175	10	--	1.290	1.5110	$\text{FCH}_2\text{CH}_2\text{OH} + \text{Cl} \text{---} \text{SO}_2 \text{---} \text{O} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_3$
$\text{FCH}_2\text{CH}_2 \text{---} \text{N} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_3 \end{array}$	107—109	760	--	0.878	1.4000	$\text{CH}_3 \text{---} \text{C}_6\text{H}_4 \text{---} \text{SO}_2 \text{---} \text{OCH}_2\text{CH}_2\text{F} + \text{HN} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_3 \end{array}$
$\text{C}_6\text{H}_5 \text{---} \text{CH}_2\text{CH}_2\text{F}$	57—60	14	--	1.064	1.4965	$\text{CH}_3 \text{---} \text{C}_6\text{H}_4 \text{---} \text{SO}_2 \text{---} \text{OCH}_2\text{CH}_2\text{F} + \text{BrMg} \text{---} \text{C}_6\text{H}_5$
$\text{O} \text{---} \text{C} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	129—131	760	--	1.362	1.4020	$\text{FCH}_2\text{CH}_2\text{OH} + \text{COCl}_2$
$\text{O} \text{---} \text{C} \begin{array}{l} \diagup \text{OCH}_2\text{CH}_2\text{F} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	95—98	16	--	1.255	1.3940	$\text{FCH}_2\text{CH}_2\text{OH} + \text{Cl} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{---} \text{OCH}_2\text{CH}_2\text{F}$
$\text{CH}_2\text{F} \text{---} \text{COOH}$	165	760	--	--	--	$\text{FCH}_2\text{CH}_2\text{OH} + \text{O}$
$\text{CH}_2\text{F} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array}$	72—75	760	--	--	--	$\text{FCH}_2\text{COONa} + \text{PCl}_5$
$\text{CH}_2\text{F} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	78—80	35	--	1.280	1.3900	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array} + \text{HgF}_2$
$\text{CH}_2\text{Cl} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	187—190	760	--	1.407	1.3900	$\text{CH}_2\text{Cl} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{FCH}_2\text{CH}_2\text{OH}$
$\text{CH}_2\text{Br} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	87—90	13	--	1.659	1.4350	$\text{CH}_2\text{Br} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{FCH}_2\text{CH}_2\text{OH}$
$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	99—105	15	--	1.991	1.5080	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{HOCH}_2\text{CH}_2\text{F}$
$\text{CH}_3 \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH}_2\text{CH}_2\text{F} \end{array}$	115—116	760	--	1.090	1.3820	$\text{CH}_3 \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{HOCH}_2\text{CH}_2\text{F}$
$\text{CH}_2\text{F} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_3 \end{array} \end{array}$	166—168	760	--	1.202	1.3980	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_3 \end{array} \end{array} + \text{HgF}_2$
$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_3 \end{array} \end{array}$	100—104	15	--	1.780	1.4918	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{HOCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_2\text{F} \end{array}$
$\text{CH}_2\text{FO} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_2\text{Cl} \end{array} \end{array}$	121	10	--	1.414	1.4295	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_2\text{Cl} \end{array} \end{array} + \text{HgF}_2$
$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_2\text{Cl} \end{array} \end{array}$	113—115	6	--	1.907	1.5180	$\text{CH}_2\text{I} \text{---} \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array} + \text{OHCH} \begin{array}{l} \diagup \text{CH}_2\text{F} \\ \diagdown \text{CH}_2\text{Cl} \end{array}$

d_{20}^{20} 1.659; n_D^{20} 1.4530; M_R 30.13.

$C_4H_8O_2BrF$. Calculated: M_R 30.11.

24; β -Fluoroethyliodoacetate. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 14 g. ethylenefluorohydrin and carefully, with cooling, 40 g. iodoacetylchloride. The reaction was completed by heating on a water-bath until the evolution of hydrogen chloride ceased. β -Fluoroethyliodoacetate was twice distilled under vacuum. Yield 40.5% of theoretical. B.p. $99-105^\circ$ at 15 mm.; reddish liquid with lachrymatory properties.

d_{20}^{20} 1.991; n_D^{20} 1.5080; M_R 37.74.

$C_4H_8O_2FI$. Calculated: M_R 35.14.

25; β -Fluoroethylacetate. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 3.2 g. ethylenefluorohydrin and gradually, with shaking, 4.8 g. acetylchloride (an excess approximately 25%). Upon completion of addition of chloroanhydride, the reaction mixture was heated on a boiling water bath until the evolution of hydrogen chloride ceased. The excess of acetylchloride was removed by distilling the reaction product over fused sodium benzoate. After repeated distillation, the b.p. of β -fluoroethylacetate: $115-116^\circ$. Yield 52% of theoretical. Colorless liquid with an ethylacetate type odor.

d_{20}^{20} 1.090; n_D^{20} 1.382; M_R 22.63.

$C_4H_7O_2F$. Calculated: M_R 22.23.

26) Fluoroisopropyl ester of fluoroacetic acid. In a flask provided with a reflux condenser were mixed 30 g. fluoroisopropyl ester of iodoacetic acid, 44 g. mercuric fluoride. The contents of the flask were heated on a boiling water bath for 6 hours, followed by heating on an oil bath at 140° for 2 hours. The metathetic reaction proceeds gradually, the color of the reaction mixture changing during the heating process from light yellow to brown. Upon completion of heating, the reaction product was extracted with dry ether. The ether was distilled off and the residue distilled under vacuum. Several distillations were then carried out under atmospheric pressure. B.p. $166-168^\circ$. Yield 40% of theoretical. Clear, colorless liquid of a weak ethereal odor.

d_{20}^{20} 1.202; n_D^{20} 1.398; M_R 27.64.

$C_5H_8O_2F_2$ Calculated: M_R 26.85.

Found: C 43.47; H 5.80.
 $C_5H_8O_2F_2$. Calculated: C 43.48; H 6.04.

27) Fluoroisopropyl ester of iodoacetic acid. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 20 g. fluoroisopropyl alcohol and carefully, with cooling, 51.4 g. of chloroanhydride of iodoacetic acid. Upon completion of addition, the reaction mixture was heated at a temperature of $40-45^\circ$ until the evolution of HCl ceased. The mixture was then cooled and the reaction product extracted with ether. The ether extract was washed with water until neutral, and then dried over fused potassium fluoride. The ether was distilled off and the residue was distilled under reduced pressure. B.p. $100-104^\circ$ at 15 mm. Yield 60% of theoretical. Light brown color, gradually darkening upon exposure to light. Strong lachrymatory properties.

d_{20}^{20} 1.7600; n_D^{20} 1.4918; M_R 40.16; %I 51.5.

$C_5H_8O_2FI$. Calculated: M_R 39.75 %I 51.7.

28) 1,3-Fluorochloroisopropyl ester of fluoroacetic acid. Into a flask provided

with a reflux condenser were introduced 41 g. 1,3-fluorochloroisopropyl iodoacetate and gradually, with shaking, a mixture of 50 g. mercuric fluoride together with 50 g. freshly ignited potassium fluoride. The reaction mixture was heated on a boiling water bath until the irritating odor present disappeared (6 hours). After completion of the reaction, fluorochloroisopropylfluoroacetate was extracted with ether. The ether was distilled off, under reduced pressure. B.p. 121° (5 mm). Yield 15%. Colorless liquid with a mild, pleasant odor.

d_{20}^{20} 1.414; n_D^{20} 1.4295; M_R^D 31.31; % Cl 21.0.

$C_5H_7O_2ClF_2$. Calculated: M_R^D 31.67 % Cl 20.58.

29) 1,3-Fluorochloroisopropyl ester of iodoacetic acid. Into a round bottom flask, provided with a reflux condenser and dropping funnel, were introduced 21 g. 1,3-fluorochloroisopropyl alcohol and gradually, with cooling 38.5 g. chloroanhydride of iodoacetic acid. Upon completion of addition, the reaction mixture was heated at a temperature of 40-50° until the evolution of HCl ceased. After cooling, the reaction product was extracted with ether. The ether extract was distilled off, and the residue redistilled under reduced pressure; after repeated distillation, b.p. 113-115° at 5 mm; yield 80% of theoretical. Reddish liquid with strong lachrymatory properties.

d_{20}^{20} 1.907; n_D^{20} 1.518; M_R^D 44.60; η_F 6.52.

$C_5H_7O_2ClFI$. Calculated: M_R^D 44.58 η_F 6.77.

CONCLUSIONS

- 1) It has been shown that ethylenechlorohydrin can be converted to ethylenefluorohydrin by means of potassium fluoride and polyfluorides. The conversion proceeds through the intermediate stage of formation of ethylene oxide.
- 2) It has been shown that potassium fluoride is capable of splitting off hydrogen chloride from chloroanhydrides and alkyl halides.
- 3) Fluorine derivatives of various groups of organic compounds have been successfully prepared by conversions from fluorohydrins: compounds prepared - fluorinated acetates, acids, ketones, amines, ethers, esters, hydrocarbons, etc.
- 4) It has been shown that synthesized β -fluoroethyl esters of sulfonic acids can be used as reagents to substitute a β -fluoroethylate group on various substances containing an active hydrogen atom.
- 5) This new method of forming a fluorocarbon bond (consisting in the interaction of aliphatic oxides with anhydrous hydrogen fluoride and its acidic salts) has extended considerably the preparation of compounds with mixed functional groups.

Submitted to the Editor

May 10, 1947

PREPARATION OF ALCOHOLS BY THE GRIGNARD REACTION USING OLEFINIC OXIDES

II. SYNTHESIS OF 2,2-DIMETHYLBUTANOL-4 AND 2,2-DIMETHYLPENTANOL-5 USING ETHYLENE OXIDE AND -6; ALSO, THE SYNTHESIS OF 2-METHYLHEXANOL-2 USING PROPYLENE OXIDE.

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The mixed magnesium organic compounds discovered by Grignard have made feasible the rapid and simple preparation of many alcohols. Many syntheses of alcohols by the action of $R\text{MgX}$ on aldehydes, ketones, and esters have been described. But few syntheses using olefin oxides have been reported, although these compounds undoubtedly can be used more extensively.

In order to extend Grignard's reaction, and also to elucidate the mechanism involved, data are given on the preparation of four alcohols using olefin oxides:

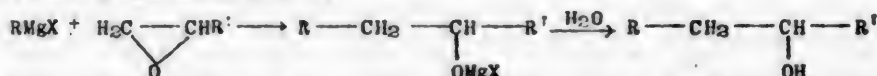
2,2-dimethylbutanol-4, from ethylene oxide and $(\text{CH}_3)_3\text{CMgCl}$;

2,2 dimethylpentanol-5, from ethylene oxide and $(\text{CH}_3)_3\text{CCH}_2\text{MgBr}$;

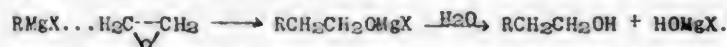
2-methanol-5, from propylene oxide and $(\text{CH}_3)_2\text{CHCH}_2\text{MgBr}$;

heptanol-2, from propylene oxide and $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{MgBr}$.

Of these 4 alcohols, 2,2-dimethylpentanol-5 is described for the first time. The alcohols were prepared as follows:

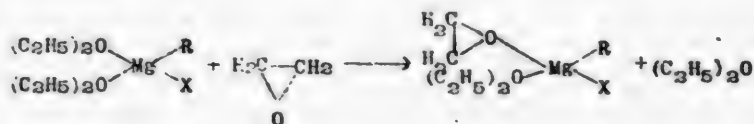


in which, for ethylene oxide, R' represents hydrogen; then with ethylene oxide primary alcohols are obtained and with propylene oxide, secondary alcohols. The formation of an alcohol by using olefin oxides and a Grignard reagent is usually represented as starting with the formation of a molecular compound of the initial substances involved. After distilling off the ether at elevated temperatures, an alcoholate is formed. The oxide ring is ruptured, and a new C-C bond is formed. After decomposing the alcoholate with water the corresponding alcohol [2] is prepared.

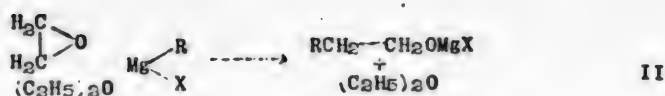


It is believed that a somewhat different mechanism may be more accurate: Ethylene oxide displaces some ether in Grignard's reagent and takes its place; when heated, after the ether is distilled off, there is a rearrangement in the new complex with a simultaneous splitting off of a second quantity of ether, which is distilled off (this is always observed at the moment of rearrangement); the alcoholate formed after rearrangement yields, on decomposition with water, the corresponding alcohol.

All this can be expressed, for example, in the case of ethylene oxide as follows:



(I)



It is of interest that by heating Grignard's reagent obtained from tertiary butyl chloride with ethylene oxide in order to accomplish the rearrangement according to equation II, a violent reaction of an explosive character is observed at 67-68°C. The reaction mixture was strongly exothermic and frequently burned out in the flask with the evolution of gray pungent smoke. In the flask remained carbon and magnesium oxide in a mixture with the halogenated salt of magnesium; therefore, in order to carry out the reaction, the ether was first distilled off at the bath temperature, not exceeding 55°, then dry toluene was introduced into the flask and the heating continued. The rearrangement was under control in the toluene solution; after treating with water 2,2-dimethylbutanol-4 was separated. In other cases the rearrangement is comparatively mild, usually accompanied by a strong foaming of reaction mixture and the distilling off ether.

EXPERIMENTAL

1. Preparation of 2,2-dimethylbutanol-4

Grignard's reagent was prepared as usual from 31 g. of tertiary butyl chloride and 12 g. magnesium shavings, in the presence of ether. The complex was then decanted from the unreacted magnesium, cooled to -10 - 12°C, and 15 g. of ethylene oxide added (in a mixture of two volumes of absolute ether). The mixture was allowed to stand for 24 hours, then the ether was distilled off on a water bath at a temperature of 55°C. After distilling off the ether a white, solid mass remained in the flask. Dry toluene (100 ml.) was added and the mixture heated on a boiling water bath for 3 hours. The muddy-green mass in the flask was cooled, decomposed with ice and acidified with hydrochloric acid. The toluene layer was separated, and the aqueous layer extracted with ether; then the toluene and ether extracts were dried with fused magnesium sulfate. After distilling off toluene the ether extract was added to the residue, ether distilled off, and the residue distilled. A fraction of a b.p. 135-143°C, in an amount of 5.0 g. was collected, and the latter yielded 4.5 g. liquid of a b.p. 140-142°C, having a pinelike odor. Yield of alcohol 13.2% of theoretical.

$$n_D^{15} 1.4323; d_4^{15} 0.844; M_{rD} 31.29$$

$$\text{C}_6\text{H}_{14}\text{O}. \text{ Calculated: } M_{rD} 31.43$$

The constants for this alcohol are not given in the literature.

$$0.1330 \text{ g. substance: } 0.3464 \text{ CO}_2; 0.1438 \text{ g. H}_2\text{O}$$

$$\text{Found \%: C } 70.04; \text{ H } 12.20$$

$$\text{C}_6\text{H}_{14}\text{O}. \text{ Calculated \%: C } 70.59; \text{ H } 12.07$$

$$0.1325 \text{ g. substance: } 30.1 \text{ ml. CH}_4 \text{ (10°, 756 mm).}$$

$$\text{Found \%: OH } 16.63$$

$$\text{C}_6\text{H}_{14}\text{O}. \text{ Calculated \%: OH } 16.66$$

In chemical properties, this compound acts as a primary alcohol (reaction with bromine and Locher-Meyer [3]); this was confirmed by oxidizing this alcohol with a chromium mixture; and aldehyde was found as confirmed by several qualitative tests (Fehling solution, ammoniacal solution of silver oxide and fuchsine-sulfurous acid).

This alcohol was synthesized by Delacre from $(\text{CH}_3)_3\text{C---CH}_2\text{CH}_2\text{Br}$ and potassium acetate [4].

2. Preparation of 2,2-dimethylpentanol-5

To Grignard's reagent usually prepared from 5 g. magnesium and 30 g. 2,2-dimethylbromopropane, ethylene oxide 9 g mixed with 20 ml. absolute ether was added while cooling

to $-10 - 12^{\circ}\text{C}$. The mixture was allowed to stand for 24 hours in ice water, and the ether was distilled off. This was followed by a strong foaming of the reaction mixture accompanied by an exothermic reaction and the distilling off of more ether. The reaction mixture was cooled and decomposed with ice water. The usual treatment followed. The distillation yielded a fraction of b.p. $155 - 162^{\circ}\text{C}$; this yielded 7 g. of a fraction of b.p. $158 - 162^{\circ}\text{C}$.

The alcohol was a colorless liquid with an odor of burnt castor oil; in small concentration it has an odor of rotten apples. Insoluble in water. miscible with alcohol and ether. Yield of alcohol 30.3% of theoretical.

$n_D^{25} 1.4315$; $d_4^{17} 0.82$; $M_D 35.76$.
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated: $M_D 36.05$.
 0.1823 g. substance: 0.4911 g. CO_2 ; 0.2250 g. H_2O .
 Found %: C 72.04; H 13.30
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated %: C 73.12; H 13.56.
 0.1270 g. substance: 26.0 ml. CH_4 (11° , 758 mm),
 Found %: OH 14.70
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated %: OH 14.73.

Urethane, m.p. 234°C . The chemical properties of the product are those of a primary alcohol (reaction with bromine, Locher-Meyer reaction [3]).

In addition, the oxidation of the alcohol with chromium mixture yields an aldehyde, as confirmed by qualitative tests with Fehling's solution and with fuchsin-sulfurous acid).

3. Preparation of 2-methylhexanol-5

To the Grignard reagent, prepared from 5 g. magnesium and 28 g. isobutyl bromide, 12 g. of propylene oxide (b.p. $36 - 38^{\circ}\text{C}$) was added, mixed with various volumes of ether. The usual treatment followed, as in the second experiment. 4.5 g. alcohol, b.p. $148 - 150^{\circ}\text{C}$, was obtained. Yield of alcohol 20% of theoretical.

$n_D^{25} 1.4231$; $d_4^{17} 0.822$; $M_D 35.84$.
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated: $M_D 36.05$.
 0.1883 g. substance: 0.4894 g. CO_2 ; 0.2344 g. H_2O .
 Found %: C 70.80; H 13.67
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated %: C 73.04; H 13.54.

The product behaved like a secondary alcohol [2]. This alcohol was first obtained by the reduction of methylisoamylketone, and then by the action of acetaldehyde on zinc diisomyl. The alcohol constants as given in the literature are:

b.p. 148 150°C and $d_4^{17} 0.8185$.

4. Preparation of Heptanol-2

Grignard's reagent was prepared from 5 g. magnesium and 28 g. butyl bromide. Propylene oxide 12 g. The subsequent operations were conducted as in the second case. Separated 6 g. alcohol b.p. $155 - 158^{\circ}\text{C}$. Yield of alcohol 30% of theoretical; alcohol has a mint-like odor, and is insoluble in water.

$n_D^{25} 1.4240$; $d_4^{17} 0.8270$; $M_D 35.60$.
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated: $M_D 36.05$.
 0.1168 g. substance: 0.3089 g. CO_2 ; 0.1429 g. H_2O .
 Found %: C 72.03; H 13.80.
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated %: C 73.04; H 13.54.
 0.1650 g. substance: 33.5 ml. CH_4 (11° , 760 mm).
 Found %: OH 14.81
 $\text{C}_7\text{H}_{16}\text{O}$. Calculated %: OH 14.73

The product behaves as a secondary alcohol. First heptanol-2 was obtained by chlorination of heptane, esterification of the chlorinated product and saponification [7]; also, from bromomagnesium amyl and acetaldehyde [8] and by the reduction of methylamylketone with sodium amalgam [9].

The constants given for the alcohol in the literature are: b.p. 157-158°C (Henry) and 158-160°C (Pickard).

d_{40}^{20} 0.8193; n_D^{20} 1.4213 (Henry).

CONCLUSIONS

1. By reacting ethylene oxide with a Grignard reagent, prepared from tertiary butyl-chloride and 2,2-dimethylbromopropane, the following alcohols have been synthesized: 2,2-dimethylbutanol-4 with a yield of 13.2% and 2,2-dimethylpentanol-5 with a yield of 33.3%; the latter is reported for the first time.

2. By reacting propylene oxide with a Grignard reagent prepared from butyl bromide and isobutyl bromide, the following alcohols have been synthesized: heptanol-2, with a yield of 30% and 2-methylhexanol-5 with a yield of 20%.

3. A more satisfactory mechanism for the formation of alcohols by the reaction of olefin oxides with Grignard's reagents has been proposed.

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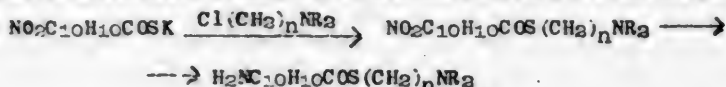
ar-4-NITRO- and ar-3-NITRO-TETRAHYDRO-1-NAPHTHALENE-CARBOETHIOLIC ACIDS,
THEIR DERIVATIVES and ALKAMINO ESTERS of ar-4-AMINO and ar-3-AMINO-
TETRAHYDRO-1-NAPHTHALENE-CARBOETHIOLIC ACIDS.

S. I. Sergievskaya and S. M. Mamiofe

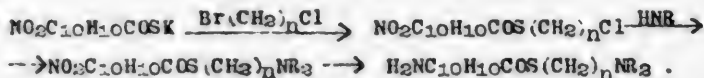
All Union Scientific-Research Chemico-Pharmaceutical Institute
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The purpose of the present investigation was the preparation of several alkamino esters: ar-4-amino- and ar-3-aminotetrahydronaphthalene-1-carboethiolic acid for test as anesthetics. In the preparation of these alkamino esters the following methods were used:

1, By the action of dialkylaminochlorides on potassium ar-nitrotetrahydronaphthalene-carboethiolate with a subsequent reduction of the nitro-group in the prepared alkaminoesters [1].



and 2, gradual building up of the ester group and the reduction of the alkaminoesters of nitrotetrahydrothionaphthene acids [2]:



The initial products not described in the literature, ar-nitrotetrahydronaphthyl-carboethiolic acid, were obtained by the action of alcoholic solution of potassium sulfohy-drate on the chloroanhydride of the corresponding ar-nitro-tetrahydronaphthoic acid (see pre-vious communications); both ar-4-nitro and ar-nitrotetrahydronaphthyl-1-carboethiolic acids represent well-defined crystalline solid substances.

In addition to several alkaminoesters, we prepared disulfides and some alkyl esters. For pharmacological testing, the hydrochlorides of diethylaminoethyl, and the diethylamino-propyl esters of ar-4-aminotetrahydronaphthalene-1-carboethiolic acid and diethyl-aminopropyl ester of ar-3-aminotetrahydronaphthalene-carboethiolic acid, were prepared.

The pharmacological testing showed that alkaminoesters of ar-4-amino-tetrahydronaphtha-lene-1-carboethiolic acid are effective anesthetics; no negative results were obtained: a 1% aqueous solution of the hydrochloride of diethylaminoethyl ester of ar-4-amino-1-tetrahydro-thionaphthoic acid caused anesthesia of the cornea in a rabbit for 40 minutes; the anesthesia started 1-3 minutes after application.

Alkaminoesters of ar-3-amino-1-tetrahydronaphthoic acid, although possessing anesthetic properties, caused irritation and hyperemia.

Acknowledgment is expressed to V. V. Zverev for the pharmacological tests.

EXPERIMENTAL

ar-4-Nitrotetrahydronaphthalene-1-carboethiolic acid

Into a three neck flask, fitted with a mechanical stirrer and thermometer, was intro-

duced an aqueous alcoholic solution of potassium hydroxide (3.4 g. KOH, 2.9 ml. water and 60 ml. ethyl alcohol). The solution was cooled to -5°C and a current of hydrogen sulfide passed in until the gain in weight was 3 g. (at -5°C)

Upon completion of saturation, a solution of potassium sulfhydrate was added gradually at a temperature of -5°C together with a solution of 6 g. of the hydrochloride of ar-4-nitro-tetrahydro-1-naphthalene carboxylic acid and 30 ml. absolute benzene.

The mixture was stirred for 10-15 minutes and then filtered. Alcohol, benzene and water were distilled off from the filtrate. The residue consisted of orange-yellow crystals of the potassium salt of ar-4-nitrotetrahydro-1-naphthalene-carbothiolic acid.*

The potassium salt was dissolved in water, filtered, and from the filtrate, by addition of 10% hydrochloric acid, the free ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid was separated. The nitrothioacid, separating as an oil, was extracted with ether; the ether solution was dried with anhydrous Na_2SO_4 and then distilled off; the remaining oily substance upon rubbing hardens rapidly to a yellow crystalline mass.

ar-4-Nitro-tetrahydro-1-naphthalene carbothiolic acid, recrystallized several times from aqueous alcohol, appeared as fine yellow crystals, m.p. $34-35^{\circ}\text{C}$, readily soluble at room temperature in alcohol, acetone, ether, and dichloroethane, and sparingly soluble in petroleum ether and water.

The nitrothioacid is quite stable in the air. Obtained: 5 g. (84% of theoretical).

4.670 mg. substance:	4.66 mg. BaSO_4
4.697 mg. substance:	4.64 mg. BaSO_4
Found %:	S 13.70, 13.57
$\text{C}_{11}\text{H}_{11}\text{O}_3\text{NS}$. Calculated %:	S 13.51

Disulfide of ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid



1) 0.3 g. ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid was dissolved in 20 ml. ethyl alcohol and through the solution was passed a current of air for 4 hours; this was then allowed to stand for several hours. A crystalline precipitate of disulfide separated. After recrystallization from dichloroethane: m.p. $163-164^{\circ}\text{C}$.

2) 0.3 g. ar-4-nitro-1-tetrahydrothionaphthoic acid was dissolved in 10 ml. ethyl alcohol, hydrochloric acid (1:1) added until acid, and slowly, dropwise, a solution of FeCl_3 ; a yellowish precipitate was formed. After recrystallization from dichloroethane m.p. $163-164^{\circ}\text{C}$.

The disulfide is readily soluble in carbon tetrachloride, readily soluble when heated in dichloroethane, and sparingly soluble in alcohol, benzene and ether.

3.920 mg. substance:	3.90 mg. BaSO_4
Found %:	S 13.66
$\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_3\text{S}_2$. Calculated %:	S 13.57.

β -Chloroethyl ester of ar-4-nitrotetrahydro-1-naphthalene-carbothiolic acid and di-(nitrotetrahydrothionaphthoyl)-ethane

Into a round bottom flask, provided with a reflux condenser, were placed a solution of 5 g. potassium ar-4-nitrotetrahydro-1-naphthalene-carbothiolate in 60 ml. ethyl alcohol and 7.5 g. freshly distilled chlorobromoethane.

* For subsequent investigations ar-4-nitro-1-tetrahydrothionaphthoic acid, as such was not isolated but its potassium salt was used in the experiments.

The potassium salt obtained after distilling off alcohol, benzene and water was dissolved in dry acetone; upon adding ether to the filtered solution, the potassium salt of the nitro acid separated out as bright yellow shiny scales. The potassium salt of ar-4-nitro-1-tetrahydrothionaphthoic acid is readily soluble in alcohol, acetone and water, but insoluble in ether.

The mixture was heated on a water bath for 4 hours at 40°C (bath temperature). When heated, the color of the solution changed from orange-red to yellow.

Upon completion of heating, potassium bromide was separated and the excess of alcohol was distilled off in vacuo. The remaining crystalline substance was recrystallized from ethyl alcohol. A portion remained undissolved and represented a side product which is described below.*

β -Chloroethyl ester of ar-4-nitrotetrahydro-1-naphthalene-carbothiolic acid appeared as colorless shiny scales (after three recrystallizations), m.p. 59-60°C. readily soluble in ether, benzene, and chloroform sparingly soluble in alcohol and insoluble in water. Obtained - 2.95 g. (50% of theoretical).

6.590 mg. substance:	3.120 mg. AgCl
5.855 mg. substance:	2.805 mg. AgCl
Found %:	Cl 11.71, 11.85
$C_{13}H_{14}O_3NClS$. Calculated %:	Cl 11.83.

β -Diethylaminoethyl ester ar-4-nitrotetrahydro-1-naphthalene-1-carbothiolic acid

Into a round bottom flask, provided with a reflux condenser, was placed 2.8 g. β -chloroethyl ester of ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid, 5.6 g. freshly distilled diethylamine and 0.1 g. sodium iodide. The mixture was heated on a water bath with slight boiling of the mixture for eight hours. Upon completion of the reaction, the mixture was poured into water, and the aqueous solution extracted with ether; the ether solution was washed with water and dried with anhydrous sodium sulfate. The ether and traces of diethylamine were distilled off. The remaining oily substance was dissolved in a small amount of absolute ether and an ether solution of hydrogen chloride carefully added: the hydrochloride of alkamino ester was separated as a crystalline substance.

The hydrochloride of diethylaminoethyl ester of ar-4-nitrotetrahydro-1-naphthalene-carbothiolic acid recrystallized twice from a mixture of alcohol and ether, appeared as colorless, shiny plates: m.p. 161-162°C. readily soluble in alcohol, acetone and water, and insoluble in ether, benzene, dichloroethane and chloroform.

3.840 mg. substance:	0.270 ml. N_2 (27°: 733 mm)
4.620 mg. substance:	0.270 ml. N_2 (28°: 732 mm)
Found %:	N 7.59, 7.71
$C_{17}H_{24}O_3N_2S \cdot HCl$. Calculated %:	N 7.51.

β -Diethylaminoethyl ester of ar-4-amino-tetrahydro-1-naphthalene carbothiolic acid

Into a three necked flask fitted with a mechanical stirrer and a reflux condenser were placed 1 g. of the hydrochloride of diethylaminoethyl ester of ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid 50 ml. 96% ethyl alcohol and 0.05 ml. hydrochloric acid of sp. gr. 1.17. The reaction mixture was heated on a water bath with stirring to 60°C (bath temperature), and at that temperature 1 g. of iron filings were added slowly over a period of 1 hour. The mixture was heated to boiling and the heating continued with stirring for 1 hour.

The mixture was allowed to settle, the alcohol solution decanted, and the precipitate of ferric hydroxide boiled twice with alcohol. The alcohol solutions were combined and filtered through a folded filter. The alcohol was distilled off in vacuo. The remaining oily substance was dissolved in water and by adding 10% sodium carbonate solution the free base was liberated, extracted with ether, and the ether solution washed with water and dried over anhydrous Na_2SO_4 . The ether solution was filtered, and from the filtrate by careful addition of an ether solution of hydrogen chloride the hydrochloride of alkamino ester was liberated.

The hydrochloride of diethylaminoethyl ester of ar-4-aminotetrahydro-1-naphthalene carbothiolic acid after recrystallization from alcohol appeared as colorless crystals of m.p. 149.5-151° readily soluble in alcohol and water and insoluble in ether.

The material insoluble in ethyl alcohol was di-nitrotetrahydrothio-naphtho(1,2)-ethane $NO_2C_{10}H_7SCOS_2C_2H_5$. After recrystallization from dichloroethane m.p. 176-177.5°C; the substance is readily soluble in chloroform, dichloroethane, and acetone, but only very slightly soluble in cold alcohol.

2.501 mg. substance: 0.186 ml N_2 (20°C, 737 mm).
 Found %: N 8.39.
 $C_{17}H_{11}ON_2S \cdot HCl$. Calculated %: N 8.18.

The citrate of diethylaminoethyl ester of ar-4-aminotetrahydro-1-naphthalene carbothiolic acid was obtained by the action of the alcohol solution of citric acid on the ether solution of the base of diethylaminoethyl ester of ar-4-aminotetrahydro-1-naphthalene carbothiolic acid. The citrate was liberated as a slightly yellow crystalline powder. Recrystallized several times from absolute ether, it melts at 119-120.3°C. The citrate of alkaminoester was readily soluble in water and alcohol and almost completely insoluble in ether and benzene.

γ-Diethylaminopropyl ester of ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid

Into a round bottom flask, provided with a reflux condenser, were placed 2.8 g. of a solution of the potassium ar-4-nitrotetrahydro-1-naphthalene carbothiolate. To the solution were added 2.4 g. of freshly distilled diethylaminopropylchloride. The mixture was heated on a water bath for 4 hours at 40°C. Upon completion of heating the precipitated potassium chloride was separated and washed with alcohol. The alcohol and traces of unreacted γ-diethylaminopropyl chloride were distilled off under vacuum, the remaining oily substance was dissolved in ether, the ether solution washed with water and dried with anhydrous sodium sulfate. The ether solution was filtered, and to the filtrate was added an ether solution of hydrogen chloride, the hydrochloride of alkaminoester being precipitated as an oil; this was then crystallized: m.p. 146-149°C. After 3 recrystallizations, first from absolute alcohol and then from 90% alcohol, the hydrochloride of γ-diethylaminopropyl ester of ar-4-nitrotetrahydro-1-naphthalene carbothiolic acid separated out as colorless crystals. m.p. 149-150°C, readily soluble in alcohol and water and insoluble in ether and benzene. Yield 1.95 g

5.940 mg. substance: 0.377 ml N_2 (15°, 746 mm).
 5.345 mg. substance: 0.402 ml N_2 (15°, 746 mm).
 7.437 mg. substance: 4.497 mg. $BaSO_4$.
 6.409 mg. substance: 3.892 mg. $BaSO_4$.
 Found %: N 7.36, 7.38; S 8.30, 8.34.
 $C_{18}H_{26}O_3N_2S \cdot HCl$. Calculated %: N 7.24; S 8.29.

γ-Diethylaminopropyl ester of ar-4-aminotetrahydro-1-naphthalene carbothiolic acid

Into a three neck flask, fitted with a mechanical stirrer and thermometer, was introduced an aqueous-alcohol solution of potassium hydroxide (2.7 g. KOH, 2.6 ml. H_2O and 45 ml. ethyl alcohol).

The solution was cooled to -5°C and a current of hydrogen sulfide passed in until there was a gain in weight of 2.7 g., the temperature being maintained at -5°C.

Upon completion of saturation, to the solution of potassium sulfohydrate, a solution of 5,3-chloranhydride of ar-3-nitro-tetrahydro-1-naphthalene carbothiolic acid in 30 ml. absolute benzene was slowly added at -5°C.

The mixture was stirred for another 10-15 minutes and filtered to separate the precipitated potassium chloride and a small amount of disulfide. Alcohol, benzene and water were distilled off under vacuum from the filtrate; the remaining yellow crystalline precipitate of the potassium ar-3-nitrotetrahydro-1-naphthalene carbothiolate was dissolved in water and filtered into a 10% solution of hydrochloric acid.*

The precipitated ar-3-nitrotetrahydro-1-naphthalene carbothiolic acid was filtered off, washed with water and recrystallized several times from ethyl alcohol. The yellowish fine crystals: m.p. 75-76°C, are readily soluble in the cold in alcohol, acetone, dichloroethane, benzene and ether, and insoluble in water. Yield: 5 g. (89.8% of theoretical).

7.965 mg. substance: 0.422 ml. N_2 (18°, 730 mm).
 7.005 mg. substance: 0.402 ml. N_2 (18°, 730 mm).
 19.63 mg. substance: 19.40 mg. $BaSO_4$.
 Found %: N 5.95, 5.97; S 13.56.
 $C_{11}H_7O_3NS$. Calculated %: N 5.91; S 13.51.

* In the subsequent reactions, instead of ar-3-nitrotetrahydro-1-naphthalene-carbothiolic acid, its potassium salt was used. The latter was obtained by the same method as potassium ar-4-nitro-1-tetrahydrothionaphthionate (See the corresponding experiment). Potassium ar-3-nitro-1-tetrahydrothionaphthionate appeared as shiny orange crystals, readily soluble in alcohol, acetone, and water, and insoluble in ether.

Disulfide of ar-3-nitrotetrahydro-1-thionaphthoic acid

a) 0.3 g. ar-3-nitro-1-tetrahydrothionaphthoic acid was dissolved in 15 ml. ethyl alcohol, the alcoholic solution filtered and a current of air passed through the filtrate for 20 hours. The separated fine crystals of disulfide were filtered off and recrystallized several times from dichloroethane. m.p.: 158-159°C.

b) Disulfide is also formed from ar-3-nitro-1-tetrahydronaphthoic acid by adding to its alcoholic solution iodine (in alcoholic solution) or a solution of FeCl_3 .

The disulfide appeared as colorless crystals, readily soluble when heated in dichloroethane or chloroform and sparingly soluble in alcohol and almost completely insoluble in ether.

11.62 mg. substance: 11.58 mg. BaSO_4 .
Found %: S 13.68
 $\text{C}_{22}\text{H}_{20}\text{O}_3\text{N}_2\text{S}_2$. Calculated %: S 13.57.

Ethyl ester of ar-3-nitrotetrahydronaphthalene-1-carbothiolic acid

1 g. of ar-3-nitrotetrahydronaphthalene-1-carbothiolic acid was dissolved in 20 ml. 0.5 n. alcoholic solution of KOH, the solution was filtered and 0.6 g. ethyl iodide added to the filtrate.

The mixture was heated on a water bath in a round-bottom flask, provided with a reflux condenser, for 3 hours at 45°C (bath temperature).

Upon completion of the reaction, potassium iodide was filtered off, and the excess of alcohol distilled off *in vacuo*.

The remaining crystalline precipitate was recrystallized several times from ethyl alcohol.

Light colorless needles of m.p. 65-66°C, readily soluble in alcohol, acetone, ether and dichloroethane and insoluble in water.

6.400 mg. substance: 0.340 ml N_2 (13.5°, 741.5 mm).
7.306 mg. substance: 0.342 ml N_2 (14°, 741.5 mm)
Found %: N 5.32, 5.43.
 $\text{C}_{13}\text{H}_{15}\text{O}_3\text{NS}$. Calculated %: N 5.28.

γ -Diethylaminopropyl ester of ar-3-nitrotetrahydronaphthalene-1-carbothiolic acid

Into a round-bottom flask, connected with a reflux condenser, was introduced a clear solution of 4 g. potassium ar-3-nitrotetrahydro-1-naphthalene carbothiolate in 100 ml. absolute ethyl alcohol. To the solution was added 2.4 g. freshly distilled γ -diethylaminopropylchloride. The mixture was heated on a water bath for 4 hours at 40°C. Upon completion of the reaction the precipitate was filtered off and the alcohol was distilled off *in vacuo* from the filtrate. The remaining oily substance was heated on a water bath under vacuum to remove traces of unreacted γ -diethylaminopropylchloride, and then dissolved in ether: the ether solution was washed with water and dried with anhydrous Na_2SO_4 .

Upon acidifying the ether solution of the base of alkamino ester with a hydrogen chloride solution the hydrochloride of γ -diethylaminopropyl ester of ar-3-nitrotetrahydro-1-naphthalene carbothiolic acid separated out as a colorless powder.

After several recrystallizations from a mixture of absolute alcohol and ether there were obtained fine crystals m.p. 177-178°C, readily soluble in ether and benzene. Yield 4.5 g.

6.885mg substance: 0.435 ml N_2 (17°, 747 mm)
8.255mg substance: 0.570 ml N_2 (17°, 747 mm)
Found %: N 7.31, 7.14.
 $\text{C}_{18}\text{H}_{23}\text{O}_3\text{N}_2\cdot\text{HCl}$. Calculated %: N 7.24.

γ -Diethylaminopropyl ester of ar-3-aminotetrahydro-1-naphthalene carbothiolic acid

Into a three-neck flask, provided with a mechanical stirrer and reflux condenser were placed 4 g. of the hydrochloride of γ -diethylaminopropyl ester of ar-3-nitrotetrahydro-1-naphthalene carbothiolic acid, 60 ml. 96% ethyl alcohol and 0.15 ml. hydrochloric acid, sp. gr. 1.17. The reaction mixture was heated on a water bath, with stirring, to 60° (bath temperature); at this temperature 2.5 g. of iron filings were slowly added over a period of 2 hours. The mixture was heated to boiling and stirred while boiling for 1 hour 30 minutes.

The precipitated ferric hydroxide was allowed to settle, the alcohol solution was decanted, and the precipitate boiled several times with alcohol. The alcoholic solutions were combined, filtered, and the alcohol was distilled off in vacuo; the remaining crystalline precipitate was recrystallized, first from absolute alcohol, then from 98% alcohol.

The hydrochloride of γ -diethylaminopropyl ester of ar-3-aminotetrahydro-1-naphthalene-carbo-
thiolic acid appeared as colorless scales, mp 168-169°C, readily soluble in water and alcohol, almost completely insoluble in ether and benzene.

The salt is soluble in water in a 1:25 ratio, aqueous solutions showing a weak alkaline reaction with litmus; it is stable on storing and does not decompose on boiling.

3.110 mg. substance.	0.214 ml. N_2 (9°, 754 mm)
4.589 mg. substance.	0.312 ml. N_2 (10.5°, 745 mm).
Found %: N 8.03.	
$C_{19}H_{23}ON_2S \cdot HCl$. Calculated %: N 7.82..	

CONCLUSIONS

1. The disulfides and esters of ar-4-nitrotetrahydro-1-naphthalene carbothiolic and ar-3-nitro-tetrahydro-1-naphthalene carbothiolic acids have been prepared.
2. Diethylaminoethyl and diethylaminopropyl esters of ar-4-aminotetrahydro-1-naphthalene carbo-
thiolic acid and diethylaminopropyl ester of ar-3-aminotetrahydro-1-naphthalene carbothiolic acid have been prepared.
3. Diethylaminoethyl ester of ar-4-aminotetrahydro-1-naphthalene carbothiolic acid possesses the best pharmacological properties.

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AMINO DERIVATIVES OF ARYLPHOSPHORIC ESTERS

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Although much is known at the present time about alkyl and aryl phosphoric esters, the diarylamino phosphonates of the type $(\text{ArO})_2\text{PONHR}$ have scarcely been investigated.

However, phosphoric esters of this type are of interest if the possibility of catalytic decomposition of the ester is considered. This has been investigated by P. Brigl and H. Müller [1] in relation to the diphenyl esters of glycerophosphoric acids and phosphofructose. It has been established by E. Zetzsche and W. Büttiker [2] that it is not always easy to split the anilide radical from the dianilidophosphoric esters by hydrolysis. This leads to the possibility that the P-N bond can be maintained when rupturing the O-Ar bond by hydrogenation. To study these possibilities we have synthesized several diarylamino phosphonates of the type $(\text{C}_6\text{H}_5\text{O})_2\text{PONHR}$ and $(\text{O}-\text{CH}_3\text{OC}_6\text{H}_4\text{O})_2\text{PONHR}$, where R is an aromatic or sulfanilamide radical.

Recent methods for the synthesis of dialkylaminophosphonates from alkylphosphites by the action upon the latter of chlorine [3] or carbon tetrachloride with the corresponding amine [4], were not extended to the diaryl phosphites. Therefore, to obtain the diarylamino phosphonates, we employed the reaction between the diphenyl ester of phosphorus monochloride, and di-(O-methoxyphenyl ester) of phosphorus monochloride with the corresponding amines, among them several sulfanilamides, according to the equation:



The reaction is carried out either in pyridine or in ether, using double the quantities of the amine indicated in the equation. The ester of the phosphorus monochloride is obtained by the condensation of phenol or guaiacol with phosphorus oxychloride [1]. The mixture of mono-, di- and tri-phenyl esters so obtained can be easily separated by a fractional vacuum distillation. To obtain the maximum yield of the diphenyl ester of phosphorus monochloride and of the di-(O-methoxyphenyl ester) of phosphorus monochloride, 1.5 moles of phenol or guaiacol is used for every mole of phosphorus oxychloride.

The various diarylamino phosphonates we obtained were easily crystallizable substances. With the exception of the sulfanilamide derivatives, they were easily soluble in ether and in a majority of the organic solvents.

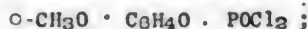
Our attempts to hydrolyze, stepwise, the diaryl-aminophosphonates were not successful. All the diarylamino phosphonates studied did not submit to the actions of acids, alkalis or catalytic reduction. In all cases there was a preferential hydrolysis of the amide bond with the formation of the diaryl esters of phosphoric acid. The analyses were carried out in our laboratory by F.V. Rosin; the analysis for phosphorus was conducted according to the method of Naiman.

EXPERIMENTAL

I. Condensation of Guaiacol with Phosphorus Trichloride

A mixture of 95 g. of POCl_3 and 117 g. of guaiacol is heated in an oil bath at $145-150^\circ$ for 4 hours, then the temperature of the bath is raised to $190-200^\circ$ and heated for another 4 hours. After cooling the product of the reaction is heated in a vacuum to drive off the excess POCl_3 , and then distilled. After a two-stage fractional distillation at 3 mm. there is obtained:

1) Mono-(O-methoxy)-phenyl ester of phosphorosodichloride



b.p. $126-129^\circ$. Weight 27 g. Active liquid, strongly fuming in air.

2) Di-(O-methoxy)-phenyl ester of phosphorosomonochloride



b.p. $213-215^\circ$, at 3 mm. Weight 51 g.

Slowly crystallizes upon standing. Recrystallized from absolute alcohol -- long, lamellated crystals, m.p. $65-67^\circ$.

0.2410 g., 0.2506 g. substance: 40.88, 41.30 ml. of 0.5 N. NaOH.

Found %: P 9.39, 9.12

$\text{C}_{18}\text{H}_{18}\text{O}_7\text{ClP}$. Calculated %: P 9.43

3) Tri-(O-methoxy) phenylphosphate: $(\text{O-CH}_3\text{O} \cdot \text{C}_6\text{H}_4\text{O})_3 \cdot \text{PO};$

b.p. $275-280^\circ$ at 3 mm. Weight 20 g. Thick syrupy, gradually crystallizing liquid. Recrystallized from methanol, m.p. $90-91^\circ$.

0.2240, 0.1798 g. substance: 30.47, 24.90 ml. 0.5 N. NaOH

Found %: P 7.53, 7.67

$\text{C}_{24}\text{H}_{27}\text{O}_{10}\text{P}$. Calculated %: P 7.74.

II. Preparation of Diphenylaminophosphonate

One mol of the diphenyl ester of phosphorosomonochloride is added dropwise and with vigorous stirring to a chilled solution of 1 mol of the amine in pyridine or a mixture of pyridine with acetone (1:2). The reaction proceeds energetically with evolution of heat. After standing at room temperature for 3-4 hours or heating for 30 minutes at $40-50^\circ\text{C}$ the reaction mixture is poured into five times its volume of cold water. The oils separating out initially slowly crystallizes upon standing. It is filtered off and washed with a 5% solution of HCl, then carefully with water, dried, and recrystallized from a suitable solvent.

1) Diphenylanilinophosphonate



Lamellated crystals from acetone or methanol. Yield 75%. M.p. $129-130^\circ$.

0.1266 g. substance 22.86 ml 0.5 N NaOH

0.1080 g. substance 4.25 ml N_2 (19° , 758 mm.)

Found %: P 10.00; N 4.49

$\text{C}_{18}\text{H}_{16}\text{O}_3\text{NP}$. Calculated %: P 9.53; N 4.30

2) Diphenyl-p-nitroanilinophosphonate



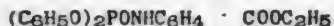
Prismatic crystals from acetone. Yield 80%. m.p. $146.5-147.5^\circ$.

0.3624, 0.3436 g. substance: 53.72, 49.87 ml 0.5 N NaOH

Found %: P 8.03, 8.02

$C_{16}H_{15}O_5N_2P$. Calculated %: P 8.37

3) Diphenyl-p-carbethoxyanilinophosphonate



From the diphenyl ester of phosphorosomono-chloride and the ethyl ester of p-aminobenzoic acid.

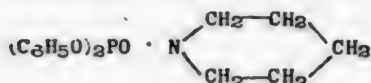
Rhombic crystals (from acetone or methanol). Yield 82%, m.p. 148.5-149°.

0.2684, 0.2770 g. substance: 36.58, 36.90 ml. 0.5 N NaOH.

Found %: P 7.54, 7.33

$C_{21}H_{20}O_5NP$. Calculated %: P 7.80

4) Diphenylpiperidylphosphonate



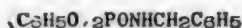
From the diphenyl ester of phosphoro mono-chloride and piperidine with a yield of 65%. Crystallizes from 85% methanol in colorless needle-shaped crystals. m.p. 75-76°.

0.1690 g. substance: 30.44 ml 0.5 N NaOH.

Found %: P 9.97

$C_{17}H_{20}O_3NP$. Calculated %: P 9.72.

5) Diphenylbenzylaminophosphonate



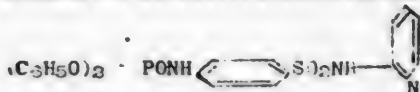
Needle shaped crystals (from ethanol). Yield 65%, m.p. 101-102.5°.

0.2154 g. substance: 36.12 ml 0.5 N NaOH.

Found %: P 9.27

$C_{19}H_{18}O_3NP$. Calculated %: P 9.17

6) Diphenyl-n-Sulfanilimidopiridylphosphonate



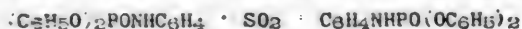
From the diphenyl ester of phosphoro mono-chloride and sulfidine with 70% yield. The product is insoluble in the usual organic solvents. It crystallizes from a mixture of benzene and pyridine (1:1) in small needles, m.p. 215-216°.

0.1146, 0.1388 g. substance: 14.06, 16.35 ml 0.5 N NaOH.

Found %: P 6.81, 6.51.

$C_{24}H_{16}O_5N_3SP$. Calculated %: P 6.44.

7) Bis-(Diphenylphosphonate, p,p'-Diaminodiphenylsulfone



From the diphenyl ester of phosphoro mono-chloride (2 mols) and p,p'-diamino-diphenylsulfone (1 mol). Yield 50-60%. Crystallizes from a mixture of ethyl alcohol and acetone (2:1) in small needles, m.p. 232-234°.

0.2348, 0.1696 g. substance: 6.94, 4.98 ml 0.1% N. HCl.
 Found %: N 4.14, 4.11.
 $C_{36}H_{30}O_8N_2SP_2$. Calculated %: N 3.93

III. Preparation of Di-(O-Methoxyphenyl) Aminophosphonate

Add dropwise with stirring and chilling an ether solution of 1 mol of di-(methoxyphenyl)-phosphorosemonochloride to an ether solution containing 2 mols of the amine. The product of the reaction is heated in a water bath for $\frac{1}{2}$ - 1 hour. The precipitated chlorohydrate of the amine is filtered, washed with ether, the ether mother-liquor evaporated to a syrupy consistency and treated with 5-6 times its volume of water. The separated oil gradually crystallizes; it is filtered off, washed with water, dried and recrystallized from a suitable solvent.

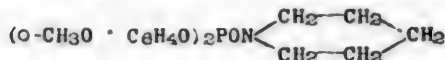
1) Di-(O-methoxyphenyl) anilinophosphate



A 65% yield for the condensation of aniline with di-(O-methoxyphenyl)-phosphorosemonochloride. Crystallizes from alcohol in needles, m.p. 129-130°.

0.2212 g. substance: 31.19 ml 0.5 N. NaOH
 Found %: P 7.80
 $C_{20}H_{20}O_5NP$. Calculated %: P 7.82.

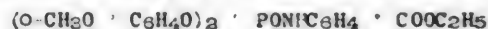
2) Di-(O-methoxyphenyl) piperidylphosphonate



By the above-described method with a 70% yield. Upon treating the product of the reaction with water, it solidifies very slowly (in 4-5 days). It is recrystallized from ether in small needle-like crystals. m.p. 55-56°.

0.1982, 0.1758 g. substance: 31.34, 27.20 ml 0.5 N. NaOH
 Found %: P 8.70, 8.57
 $C_{19}H_{24}O_5NP$. Calculated %: P 8.22.

3) Di-(O-methoxyphenyl) p-carbethoxyphenylaminophosphonate



Yield 70%. Crystallizes from ethanol or acetone in needles, m.p. 108-109°C.

0.2097, 0.2106 g. substance: 27.56, 24.88 ml. 0.5 N NaOH
 Found %: P 6.48, 6.54
 $C_{23}H_{24}O_7NP$. Calculated %: P 6.78.

CONCLUSIONS

1. Diarylamminophosphonates of the type $(C_6H_5O)_2 \cdot PONHR$ and $(O-CH_3O \cdot C_6H_4O)_2PONHR$ where R- is the aromatic or sulfamide radical, have been prepared.

2. The diarylamminophosphonates prepared produce diaryl esters of phosphoric acid upon hydrolysis or catalytic reduction and under these conditions the preservation of the phosphamide bond was not realized.

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CLEAVAGE OF AROMATIC ARSINES BY ACYL CHLORIDES

IN THE PRESENCE OF ALUMINUM CHLORIDE

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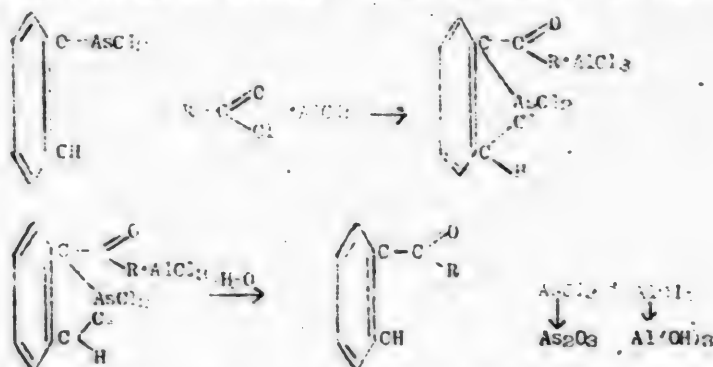
In 1935 we found that phenyldichloroarsine, diphenylchloroarsine and diphenylcyanarsine upon being heated in a solution of carbon disulfide with acetyl chloride or with the oxychloride of chloroacetic acid or with acetic anhydride in the presence of anhydrous aluminum chloride form acetophenone or chloroacetophenone in good yields [1].

The ease of splitting off arsenic from the benzene ring was utilized by us as a method for the determination of the structure of substituted halogenoarsines, since the acetyl group entered in the place of arsenic. Acetophenone or its substituted product thus obtained could be identified as such or could be oxidized into derivatives of benzoic acid; the latter was used for the identification of the compounds of arsenic. Also, in a continuation of this investigation in 1936, we converted p-nitrophenyldichloroarsine to p-nitroacetophenone, and p-chlorophenyldichloroarsine to p-chloroacetophenone. [2].

We can now report the data on the cleavage of phenyldichloroarsine to diphenylchloroarsine in the presence of aluminum chloride by using the oxychlorides of these acids, propionic, n-butyric, isovaleric. Some theoretical considerations dealing with these are also discussed, as well as some earlier-published reactions.

At first glance it appears that aluminum chloride forms a complex with the oxychloride which then reacts with arsine. The complex is added to the arsine in a manner similar to the addition of the acyl radical to carbon, shifting arsenic, and chlorine from the oxychloride to the adjacent carbon. Aluminum chloride remains in a combined state with the resulting compound. When the complex is treated with water it splits off arsenic chloride from the benzene ring; thus, depending on the oxychloride used, acetophenone or another fatty aromatic ketone may be formed.

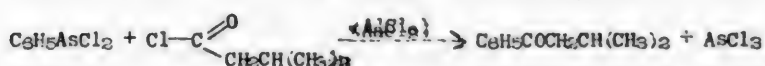
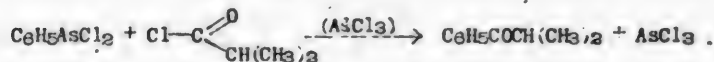
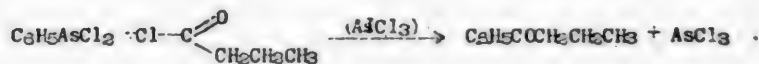
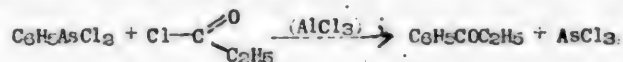
By taking halogen-arsine with substituents in the benzene ring, the correspondingly substituted fatty aromatic ketones are obtained. The whole process can be, generally, expressed as follows:



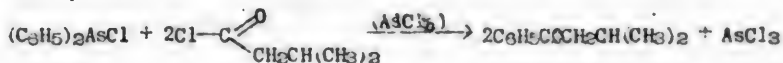
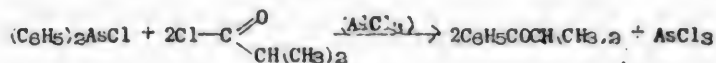
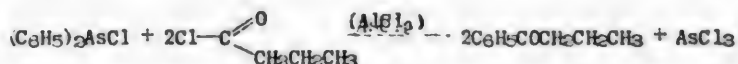
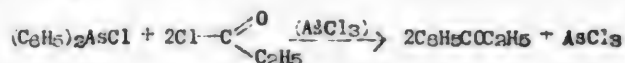
Thus, the suggested scheme in general resembles the mechanism for the formation of ketone,

according to Wieland [3] in the Friedel-Crafts reaction.

By reacting phenylchloroarsine in the presence of carbon disulfide with the oxychlorides of isovaleric, n-butyric, isobutyric and propionic acids, in the presence of aluminum chloride, the following fatty aromatic ketones were obtained in yields from 68-70%: n-propylphenylketone, isopropylphenylketone, ethylphenylketone, primary isobutylphenylketone, according to the schemes:



From diphenylchloroarsine in the presence of aluminum chloride in carbon disulfide solution with the same oxychlorides, the previously mentioned ketones were obtained with yields ranging from 60 to 67%, according to the schemes:



1) Action of oxychloride of isovaleric acid on phenyldichloroarsine

To a mixture of 8.4 g. (1/30 g.-mole), phenyldichloroarsine, 40 g. dry carbon disulfide, and 6 g. (small excess above theoretical) anhydrous aluminum chloride, placed in a flask with a vertical condenser, was added dropwise over a period of 20 minutes. 5 g. of the oxychloride of isovaleric acid, b.p. 115°C. The flask was cooled with snow. Upon the addition of the oxychloride the mixture was allowed to remain in snow for 30 minutes, and then heated on a water bath until the evolution of hydrogen chloride ceased. After 2 - 2.5 hours of heating the carbon disulfide was distilled off. In the flask remained a dark gray syrupy mass, which was poured into ice water, in small portions, with stirring. On the bottom of the glass was collected a dry oil with an odor resembling that of isobutylphenylketone. The ketone was extracted with ether and the ether solution was dried with calcium chloride. After distilling off the ether the residue was distilled, the temperature rose rapidly, and at 220-232°C. 4.3 g. of liquid having the properties of a ketone was collected. After repeated distillation, 4 g. of ketone was obtained, b.p. 229-230°. Yield of pure ketone is 69% of theoretical, (of technical 74.1%). m.p. of oxime 73-74°.

2) Action of oxychloride of n-butyric acid on phenyldichloroarsine

Quantities used: phenyldichloroarsine 5.7 g (1/40 g.-mole), oxychloride of n-butyric acid 3 g. (small excess above 1/40 g.-mole); b.p. 100-102°C, aluminum chloride 3.5 g, carbon disulfide 30 g. The experiment was conducted as in the first case. After distilling off the ether, a ketone fraction was collected in the interval 220-226°C. Yield 2.8 g. ketone, 73.7% of theoretical. M.p. of oxime 48-49.5°C.

3) Action of oxychloride of isobutyric acid on phenyldichloroarsine

Phenyldichloroarsine: 5.7 g. (1/40 g.-mole). The other substances were taken in the same amounts as in the second experiment. B.p. of oxychloride: 92°. The experiment was conducted as in the first case. Yield 2.6 g. ketone: b.p. 213-217°. Yield 68.4% of theoretical. m.p. of oxime 57-58°C.

4) Action of oxychloride of propionic acid on phenyldichloroarsine.

Taken: 5.7 g phenyldichloroarsine, 3 g. oxychloride of propionic acid of b.p. 80°C, aluminum chloride 3.5 g., carbon disulfide 30 g.

The experiment was conducted as in the first case. Yield 2.6 g. ketone: b.p. 206-210°C. Yield of ethylphenylketone: 76.5%. M.p. of oxime 49-50°.

5) Action of oxychloride of isovaleric acid on diphenylchloroarsine

13.2 g. diphenylchloroarsine (1/20 g.-mole) was dissolved in 60 g. dry carbon disulfide and added to a solution of 13.8 g. of anhydrous aluminum chloride (1/10 g.-mole). The splitting off arsenic is carried out by using 12.5 g. oxychloride of isovaleric acid: b.p. 115°C. The experiment was conducted as in the first case. Yield 10 g. isobutylphenylketone: b.p. 228-232°C. Yield 61.7%. M.p. of oxime 73.5-75°C.

6) The action of oxychloride of n. butyric acid on diphenylchloroarsine

Taken diphenylchloroarsine 13.2 g., oxychloride - b.p. 101°C - 11 g., aluminum chloride 13.3 g., carbon disulfide 60 g.. Yield 10.0 g. propylphenylketone: b.p. 220-226°. Yield 67.5%. B. p. of the oxime 49-50°C.

7) Action of oxychloride of isobutyric acid on diphenylchloroarsine

Taken diphenylchloroarsine: 6.6 g., oxychloride of isobutyric acid of b.p. 92°C - 5.5 g., aluminum chloride 6.5 g., carbon disulfide 30 g.

The experiment was conducted as in the first case. Yield 4.5 g. isopropylphenylketone: b.p. 214-218°C. Yield of ketone 60%. M.p. of oxime 57-57.5°.

8) Action of oxychloride of propionic acid on diphenylchloroarsine

Taken: 6.6 g. diphenylchloroarsine, 5 g. oxychloride of propionic acid - b.p. 80°C, 6.5 g. aluminum chloride, 30 g. carbon disulfide. Experiment conducted as in the previous cases. Yield 4.3 g ethylphenylketone b.p. 206-210°C. Yield of ketone 65%. M.p. of oxime 49-50°C.

CONCLUSIONS

1. Phenyldichloroarsine and diphenylchloroarsine, in reaction with oxychlorides of the following acids propionic, butyric, isobutyric, isovaleric, and in the presence of aluminum chloride, split off arsenic, and as a result form the corresponding fatty aromatic ketones.

2. The formation of the ketones from halogen substituted arsines or their substituted compounds permits a ready determination of the point of arsenic attachment, since the latter is displaced when the ketone group is formed.

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Submitted to the editor April 14, 1947.

SYNTHESIS OF AMINOSULFONES

I: p-AMINOPHENYLDIALKYLAMINOALKYLSULFONES *

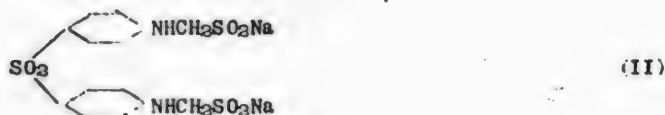
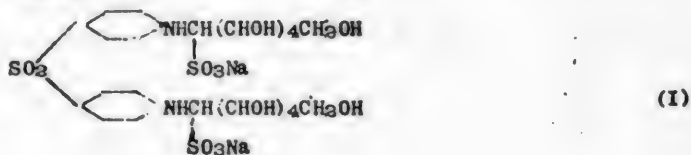
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Scientific Research Chemico-Pharmaceutical Institute (Ortzhonikidze Memorial), Moscow

The American investigators Hinshau and Feldman [1] pointed out recently that up to 1940 none of the antitubercular remedies tested in chemotherapy were effective in stopping the development of the disease in experimentally inoculated guinea pigs.

The first compound of this kind was promiae (I) p,p'-diaminophenyl-N,N'-diglucosulfonate. In addition to this preparation, only a few others reached the clinical stage: diazone (II) (p,p'-diformaldehydesulfoxylate of sodium-diaminodiphenylsulfone), promizol (III) (4,4'-diaminophenyl-5'-thiazolylsulfone) and streptomycin.

Omitting the antibiotic, streptomycin, since its structure is being investigated at present, the other preparations are derivatives of 4,4'-diaminodiphenylsulfone or its heterocyclic analogs. The given compounds:



have not been promising as remedies for curing tuberculosis. For this purpose their toxicity proved much too high in comparison with their chemotherapeutical activity. However, some of the given compounds, including 4,4'-diaminodiphenylsulfone and its diacetyl derivative, were found to be active against a series of other infectious diseases. They are used as "para-tubercular" remedies, i.e., those effective against secondary infections in tuberculosis.**

* Extensive research work on the synthesis and study of various aminosulfones had started during the war. Wartime and early postwar conditions hindered a regular exchange of scientific literature; it was only after considerable delay, therefore, that we learned about the synthesis of these compounds abroad. Since we obtained a number of amino-sulfones and their intermediate products by a method different from that reported, we are publishing this article as a preliminary communication.

** For this purpose, the Medical Soviet of the Office of the Peoples' Health Protection approved the use of 4,4'-diacetyldiaminodiphenylsulfone under the name of sulfodiamin.

At the same time the fact that such remedies are available, which act specifically against tuberculosis in living organisms, stimulated many investigators, in Europe and abroad, to work on the chemical development and investigation of various aminosulfones [10-11].

In 1936 a French patent [12] was published which claimed, among other details, a method for the preparation of p aminophenyl β diethylaminoethylsulfone. The method consisted in boiling sodium p acetylamino benzolsulfinate in a solution of metallic sodium in alcohol with the hydrochloride of β diethylaminoethylchloride. It is stated that an oily product is formed which crystallizes only after long standing. No data on physical and chemical properties of the obtained substances are given by the authors.

Last year Goldberg [9] published an article in which he described a complicated method of preparing the dihydrochloride of p aminophenyl- γ -diethylaminopropylsulfone (IV):



As a result of a series of reactions, in which individual intermediate products were not isolated, the author prepared an oily product, which could not be crystallized.

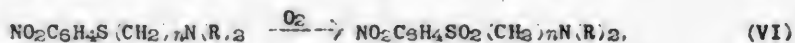
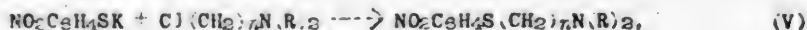
By using hydrogen chloride gas, an extremely hygroscopic dihydrochloride was obtained, m.p. 180-186°C. The analytical data for this compound are inexact. Thus, the chlorine content is 1.6% less, and that of sulfur 0.7% more than theoretical. In the same year Walker [13] published a paper in which is described the syntheses of the dihydrochloride of p aminophenyl β -diethylaminoethylsulfone and the sulfate of p aminophenyl- γ diethylaminopropylsulfone.

Following the method of preparation of sulfones, as described by Otto, by the condensation of alkaline salts of phenylsulfonic acid with the chlorides of the corresponding amines, the expected results were not obtained. Walker failed to isolate the individual bases. He obtained oily products and converted them to salts, giving their analyses and constants.

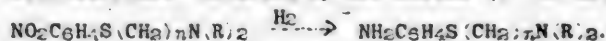
The present investigation started with the condensation of potassium p-acetylamino-phenylsulfinate with β diethylaminoethylchloride, but a crystalline product, m.p. 285-287°C, was obtained.

The analytical data for this substance for nitrogen and sulfur showed that the desired substance was not obtained (see details below). Later it was found that Goldberg and Besly, [8], using the same method, also obtained a product of m.p. 284°C.

Failing to obtain the desired products by this method, an attempt was made to condense potassium p-nitrophenylmercaptide with the corresponding dialkylaminoalkyl chlorides. The sulfides obtained were oxidized to sulfones, and a subsequent reduction of sulfones yielded the desired diamines according to the scheme:



As a result of reactions (V), (VI) and (VII), individual chemical substances were obtained; their composition and structure were elucidated from the analyses and the method of preparation. For a more complete proof of the identity of the substances, an attempt was made to reduce the "nitrosulfides" obtained by the scheme (V) to aminosulfides (VIII):



(VIII)

EXPERIMENTAL

1. β -Diethylaminoethylchloride *



To a mixture of 58.5 g. diethylaminoethanol with 15 ml. dichloroethane, with stirring and maintaining of the bath temperature at 40°C, there was added gradually a mixture of 55 ml. phosphorus trichloride with 20 ml. dichloroethane. Upon completion of addition, the reaction mixture was stirred for 6 hours at its boiling point. The excess of phosphorous trichloride and dichloroethane was distilled off *in vacuo*; the remainder, a solid, bright orange mass, was diluted with 50 ml. water and filtered off from the phosphorous compounds.

The filtrate was made alkaline to phenolphthalein by using a 50% solution of NaOH. The liberated chloride, a colorless clear liquid, was dried with anhydrous sodium sulfate. Yield 55 g. (80%).

2. β -Dimethylaminoethylchloride *



This preparation was under the same conditions as those used for β -ethylaminoethylchloride. For this reaction 55 g. dimethylaminoethanol and 64 ml. phosphorus trichloride were used. Yield 45 g. (68%).

3. Condensation of β -diethylaminoethylchloride with the potassium salt of p-acetylaminobenzenesulfonic acid **

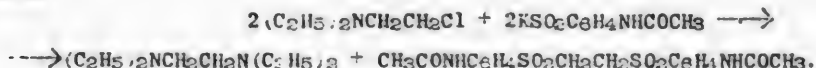
4.74 g. of potassium p-acetylaminobenzenesulfinate was heated to boiling in 30 ml. alcohol. To the boiling solution was added 3.0 g. of β -diethylaminoethylchloride. The solution was maintained at its boiling point for 5 hours. Upon completion of the reaction, the precipitate was filtered off and washed with water. It was found to be insoluble in most of the organic solvents, with the exception of glacial acetic acid.

After recrystallization from acetic acid, the crystals melted at 285-287°. According to the analysis for nitrogen and sulfur, it contained: N 6.83%; S 15.3%. The analysis indicates that the desired sulfone was not obtained. Goldberg and Besby [8] by using the same method obtained a compound of m.p. 284°. They ascribed to it the structure (IX):



Theoretically the substance contains: N 6.6%; S 15.1%.

According to these investigators, the reaction proceeds according to the following scheme:



4. p-nitrophenyl- β -dimethylaminoethylsulfide



6.8 g. KOH was dissolved in 150 ml. alcohol. To the solution was added 21 g. p-nitrophenylmercaptan (10% excess). p-Nitrophenylmercaptan was prepared by the procedure of Zincke and Lenhardt [24]. The entire mixture was heated to the boiling point of the alcohol. To the boiling solution was gradually added through a dropping funnel 13.3 g. β -dimethylaminoethylchloride. On adding the chloride, KCl precipitated and the solution became clear. The reaction was considered complete when the solution changed from a dark red color to a light yellow. The mixture was cooled, potassium chloride filtered off, half of the volume of alcohol distilled off from the filtrate, and the remaining amount poured into 300 ml. water. A light

* Dialkylaminoalkylchlorides, according to the literature data were obtained by different investigators either by prolonged heating of the corresponding alcohols with hydrogen chloride, or by means of thionylchloride.

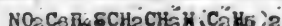
** p-acetylaminosulfonic acid was prepared by the procedure given in "Organic Syntheses" Vol I., GRIFFIN 1932, p. 30.

brown oily substance was isolated. It was extracted with ether, the ether extract dried with anhydrous potassium carbonate, and the ether distilled off. Yield 19.0 g. (68%) of sulfide as a red oily liquid.

The sulfide is readily soluble in ordinary organic solvents, immiscible with water, and cannot be distilled in vacuo. With hydrochloric acid it gives a hydrochloride of m.p. 215-217°C. (after recrystallization from alcohol).

Found %: S 12.18; N 10.79
 $C_{10}H_{15}O_2N_2ClS$. Calculated %: S 12.18; N 10.67

5. p-Nitrophenyl-β-diethylaminoethylsulfide



The condensation reaction of p-nitrophenylmercaptan with β-diethylaminoethylchloride was carried out in the same manner as with β-dimethylaminoethylchloride. To the solution of 13.8 g. mercaptan (10% excess) and alkali alcoholate (4.5 g. KOH and 100 ml. alcohol) was gradually added 11 g. β-diethylaminoethylchloride. Yield 16 g. (77%) sulfide. This sulfide did not crystallize also and according to all its other properties was similar to p-nitrophenyl β-dimethylaminoethylsulfide. In a reaction with hydrochloric acid it yielded a hydrochloride sparingly soluble in water, m.p. 172-174°C (after recrystallization from alcohol).

Found %: S 11.42; N 9.49
 $C_{12}H_{19}O_2N_2ClS$. Calculated %: S 11.01; N 9.64.

6. p-Nitrophenyl-γ-diethylaminopropylsulfide



The condensation of p-nitrophenylmercaptan with γ-diethylaminopropylchloride was conducted as in the previous condensations.

To a solution of 13.8 g. (10% excess) of mercaptan in alkali alcoholate (4.59 g. KOH and 100 ml. alcohol) was added 12.2 g. γ-diethylaminopropylchloride.

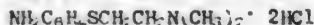
Yield 16.4 g. (75%) sulfide. The sulfide forms highly water-soluble hydrochloride. Because of this difference from its lower homologs it was liberated from the hydrochloric acid solution by using a 10% sodium hydroxide solution. The liberated oily product was extracted with ether; after distilling off the ether, a liquid product was obtained which on analysis for sulfur showed good agreement:

Found %: S 11.72
 $C_{13}H_{21}O_2N_2S$. Calculated %: S 11.93.

The sulfide was soluble in ether. By using an alcoholic solution of hydrogen chloride, the hydrochloride of p-nitrophenyl-γ-diethylamino-propylsulfide of m.p. 146-148°C was separated.

Found %: S 10.64; N 8.8
 $C_{15}H_{23}O_2N_2ClS$. Calculated %: S 10.5; N 9.19

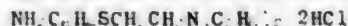
7. Dihydrochloride of p-aminophenyl-β-dimethylamino ethyl sulfide



The reduction of p-nitrophenyl β-dimethylaminoethylsulfide was conducted catalytically by active hydrogen in the presence of Raney catalyst at room temperature and under atmospheric pressure. For catalysis, 5 g. of the nitroproduct in 20 ml. of alcohol was taken. As a result there was obtained 3.5 g. (81.7%) of the aminopropuct as an oily, colorless, non-crystallizing liquid. By using absolute ether and alcoholic hydrochloric acid, the dehydrochloride amino sulfide was obtained. After recrystallization from absolute alcohol, this melted at 222-224°C.

Found %: Cl 26.37; N 10.19
 $C_{10}H_{16}N_2Cl_2S$. Calculated %: Cl 26.39; N 10.40.

8. Dihydrochloride of p-aminophenyl β-diethylaminoethylsulfide



The reduction of p-nitrophenyl β-diethylaminoethylsulfide was carried out catalytically

by using active hydrogen under the conditions of the earlier experiment. 4 g. of sulfide was dissolved in 20 ml. alcohol. The reduction yielded 3.3 g. (94%) of an oily, colorless substance. The product was dissolved in ether, and by using alcoholic hydrogen chloride an extremely hygroscopic dihydrochloride was separated. After drying it in a vacuum-desiccator the dihydrochloride was dissolved in absolute alcohol; the solution was filtered, and the hydrochloride liberated by using absolute ether. A crystalline substance, m.p. 186 - 188°C. was obtained. This, upon crystallization from absolute ether, yielded crystals of m.p. 188-190°C.

Found %: N 9.57; Cl 23.97
 $C_{12}H_{22}N_2Cl_2S$. Calculated %: N 9.43; Cl 23.90

9. Dihydrochloride of p-aminophenyl-γ-diethylaminopropylsulfide



The reduction of p-nitrophenyl-γ-diethylaminopropylsulfide was carried out by using hydrogen in the presence of a Raney nickel catalyst under conditions given previously. From 4 g. of the nitroproduct, there was obtained 3 g. (85%) of an oily, colorless substance. After purification, similar to that conducted in the earlier experiment, there was obtained a dihydrochloride of p-aminophenyl-γ-diethylaminopropylsulfide of m.p. 161-163°C.

Found %: N 8.86; Cl 22.97
 $C_{13}H_{24}N_2Cl_2S$. Calculated %: N 9.00; Cl 22.83

10 p-Nitrophenyl β-dimethylaminoethylsulfone



15 g. of the hydrochloride of p-nitrophenyl-β-dimethylaminoethylsulfide was dissolved in 105 ml. glacial acetic acid. To the solution, heated to 70°C, with stirring, was gradually added through a dropping funnel 21 ml. 28% hydrogen peroxide. Upon completion of addition of hydrogen peroxide, the solution was heated for another 2 hours at a temperature of 75-80°C. Then the solution was made alkaline to phenolphthalein using a 10% solution of sodium hydroxide. p-Nitrophenyl β-dimethylaminoethylsulfone was separated as a yellow crystalline precipitate. It was filtered on a Buchner funnel using suction, and washed with water. Weight of precipitate, 11 g. (75%).

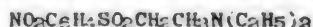
For purification, the product was recrystallized from alcohol or ether. The pure product melted at a temperature of 109-110°C.

Found %: S 12.22; N 10.60
 $C_{12}H_{15}O_4N_2S$. Calculated %: S 12.4; N 10.85

Dissolving this in ether and treating it with an alcoholic solution of hydrogen chloride produced a hydrochloride of m.p. 199-201°C.

Found %: S 11.01; N 9.4
 $C_{12}H_{15}O_4N_2ClS$. Calculated %: S 10.86; N 9.51

11. p-Nitrophenyl β-diethylaminoethylsulfone



The preparation of p-nitrophenyl β-diethylaminoethylsulfone was carried out under the same conditions as the preparation of p-nitrophenyl β-dimethylaminoethylsulfone. For the reaction were taken 21 g. of the hydrochloride of p-nitrophenyl β-diethylaminoethylsulfide, 145 ml. glacial acetic acid and 26 ml. 28% hydrogen peroxide.

Yield 15 g. (72%) of golden-yellow crystals. For purification the substance was recrystallized from ether or alcohol. Pure product melts at 93-95°C.

Found %: S 11.38; N 9.88
 $C_{14}H_{19}O_4N_2S$. Calculated %: S 11.19; N 9.79

Dissolving in ether and treating with alcoholic solution of hydrogen chloride yields

the hydrochloride. m.p. 185-187°C.

Found %: S 9.73; N 8.45
C₁₂H₁₃O₄N₂ClS. Calculated %: S 9.92; N 8.68.

12. p Nitrophenyl γ diethylaminopropylsulfone



24 g. of p-nitrophenyl-γ-diethylaminopropylsulfide was dissolved in 100 ml. glacial acetic acid. To a solution, heated to 70°C. was added 30 ml. 28% hydrogen peroxide. Upon completion of the reaction and neutralization, nitrosulfone was obtained as oily yellow crystals. This precipitate was extracted with ether; the ether extract was dried, and the ether distilled off. The residual mass crystallized on cooling as yellow crystals. Yield 19 g. (70%). The substance is readily soluble in ordinary organic solvents. After recrystallization from ligroin or aqueous alcohol (2:1) it melts at 57-59°C.

Found %: C 52.16; H 6.57; N 9.60.
C₁₅H₁₉O₄N₂S. Calculated %: C 52.00; H 6.66; N 9.33.

of hydrochloride 191-193°C.

Found %: S 9.51; N 8.64.
C₁₅H₂₁O₄N₂ClS. Calculated %: S 9.50; N 8.32.

13. p-Aminophenyl β-dimethylaminoethylsulfone



a) Reduction with iron in neutral medium 0.80 g. of ammonium chloride was dissolved in 50 ml. water at 70°C. At this temperature 4.3 g. reduced iron was added to the solution. Then gradually, with efficient stirring, 2 g. of p nitrophenyl β dimethylaminoethylsulfone was added. After adding the entire nitro compound the reaction mixture was stirred for another 6 hours, then cooled, and the slimy mixture filtered off.

An acetone extraction of this slimy mixture yielded 0.3 g. (17%) of a crystalline substance, m.p. 169-171°C. An ether extraction of the aqueous filtrate yielded 0.7 g. (41%) of another crystalline substance, m.p. 137-138°C. The substance of m.p. 137-138°C represents the desired sulfone. It is soluble in all ordinary organic solvents and in water. The sulfone contains a free amino group (qualitative reaction).

Found %: C 52.95; H 6.97; N 12.02; S 13.76.
C₁₁H₁₅O₂N₂S. Calculated %: C 52.63; H 7.01; N 12.28; S 14.03.

The second substance of m.p. 169-171°C was also analyzed for carbon, hydrogen, nitrogen and sulfur.

Found %: C 50.83; H 5.29; N 11.03; S 16.88.

Its structure has not yet been determined.

b) Reduction with hydrogen in the presence of nickel Raney catalyst. For this reduction 1 g. p nitrophenyl β-dimethylaminoethylsulfone, 2 g. catalyst and 60 ml. alcohol were taken. The reduction was carried out at room temperature and at atmospheric pressure. Yield 0.85 g. (95%). After recrystallization from alcohol the substance melted at 137-138°C and gave no melting point depression with the substance separated from the aqueous filtrate in the reduction with iron.

14. p Aminophenyl β diethylaminoethylsulfone



a) Reduction with iron in a neutral medium. The reaction was carried out under the same conditions as the reduction of p nitrophenyl β dimethylaminoethylsulfone.

There were taken 3 g. p nitrophenyl β diethylaminoethylsulfone, 5 g. reduced iron, 0.8 g. ammonium chloride and 55 ml. water. The reaction was carried out for 3 hours. As a result of this reaction, the slimy product yielded a substance of m.p. 171-172°C, insoluble

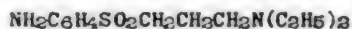
in water. Yield 0.7 g (34%). This substance gives no depression when melted with the substance isolated from the slimy product in the reduction of p-nitrophenyl-β-dimethylaminoethylsulfone (see above).

From the aqueous filtrate, by ether extraction, there was liberated another substance of m.p. 98-100°C. representing, as shown by elemental analysis, the desired aminosulfone (after crystallization from alcohol). It is soluble at room temperature in acetone and benzene; it is sparingly soluble in ether and water; insoluble in petroleum ether.

Found %: C 56.39; H 7.84; N 10.93 S 12.64.
 $C_{12}H_{20}O_2N_2S$. Calculated %: C 56.25; H 7.8; N 10.93 S 12.50

b) Reduction with hydrogen in the presence of Raney nickel catalyst. For reduction, 1 g. p-nitrophenyl-β-diethylaminoethylsulfone was dissolved in 60 ml. alcohol, and 3 g. of catalyst added. The reduction was carried out at room temperature and atmospheric pressure. Produced -- crystalline substance. Yield 0.8 g. (90%); m.p. 98-100°C. A mixed sample of this substance with that separated from the aqueous filtrate, in the reduction with iron, gave no depression of the melting point.

15. p-Aminophenyl-γ-diethylaminopropylsulfone



a, Reduction with iron in neutral medium. The reaction was carried out under the same conditions as given above. The reaction time, however, was extended to 6 hours. Taken: 10 g p-nitrophenyl γ-diethylaminopropylsulfone, 20 g. reduced iron 3 g. ammonium chloride and 200 ml. water.

Upon completion of the reaction neither a reduction product nor the initial intermediate was found in the slimy residue. The aqueous filtrate gave upon extraction with ether 5 g. (55%) of a crystalline substance. The substance is readily soluble in ordinary organic solvents, with the exception of petroleum ether. For purification it was dissolved in ether and then precipitated with petroleum ether. The desired diamine of m.p. 78-79°C was obtained.

Found %: C 57.73; H 8.31; N 10.5
 $C_{13}H_{22}O_2N_2S$. Calculated %: C 57.78; H 8.14; N 10.36.

b) Reduction with hydrogen in the presence of Raney nickel catalyst. For reduction, 1 g. of p-nitrophenyl γ-diethylaminopropylsulfone was dissolved in 25 ml. alcohol and 2 g. of catalyst added. The reduction was carried out at atmospheric pressure and room temperature.

The product obtained as a result of reduction was dissolved in ether and precipitated with petroleum ether. A substance was obtained of a m.p. 78-79°C in an amount of 0.8 g. (89%). This substance gives no depression when melted with a mixed sample with the substance obtained in the reduction with iron.

CONCLUSIONS

1. Twelve individual products in the series of p-aminophenyldialkylaminoalkylsulfones have been synthesized and characterized.
2. The dialkylaminoalkylchlorides used for the synthesis were obtained by treating the corresponding alcohols with phosphorus trichloride.
3. The reduction of the compounds (sulfones and sulfides) was carried out by the method of catalytic reduction in the presence of a Raney nickel catalyst.

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 April 12, 1947

O-ETHERS OF LUPININE

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In earlier papers [1,2] new methods of separating lupinine from anabasine-sulfate were reported.

The present article discusses the synthesis of the derivatives of lupinine.

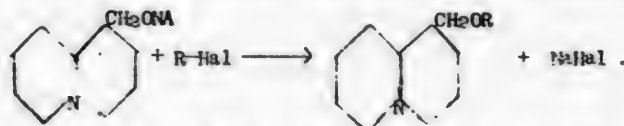
Some of the derivatives of lupinine were obtained by Katsnelson and Kabachnik [3], who synthesized the ester of p-aminobenzoic acid and lupinine, named by them lupicain. These authors obtained a series of derivatives of lupinyl-barbituric acid. The pharmacological study of lupicain showed that it is an anesthetic. Recently Panashchenko [4] carried out a pharmacological investigation of lupinine in comparison with lupicain. He concluded that lupinine differed from lupicain in that the former displays no local anesthetic action.

Knun'yants and Benevolenskaya [5] synthesized various lupinine analogs of plasmochin, atebrin, and 2-methylmethoxybenzothiazole. These substances were found to exhibit low toxicity, and were fairly active against malarial plasmodia.

We have also synthesized lupicain using another method: starting with sodium lupinate and the chloromethylene of p-nitrobenzoic acid.

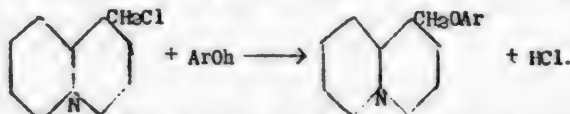
In addition, a series of O-ethers of lupinine with radicals of fatty and aromatic groups have been obtained. To synthesize ethers with fatty radicals, we started with equimolar amounts of sodium lupinate and alkyl halides in a solution of the respective alcohols.

The reaction was carried out with boiling for 3-5 hours; after distilling off the solvent the product was purified by recrystallization. The equation for the reaction may be represented as follows:

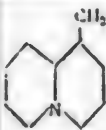

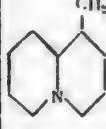


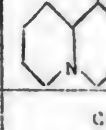

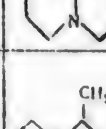



For the first four radicals (CH₃, C₂H₅, C₃H₇, C₄H₉) the ethers obtained crystallize from acetone as colorless crystals, yielding salts; these are readily soluble in water and in ordinary organic solvents, and remain unchanged on long storing. A qualitative test for the presence of halogen in the preparations was negative.

The ethers of aromatic series, and also the ether of diethylaminoethanol, were synthesized from chlorolupinan and the corresponding hydroxyl-containing compounds according to the following equation:



Equimolar amounts of the initial products were heated in the presence of potassium hydroxide at a temperature of 130-140°C for 3-4 hours on an oil bath or in a sealed tube. The following were obtained: phenyl, cresyl (o- and p-), naphthyl (α-), ethers of lupinine and the ether of diethylaminoethanol. All ethers, with the exception of the phenyl and of diethylaminoethanol, are crystalline substances which give well defined crystalline picrates and iodomethylates. They are readily soluble

No.	Name	Formula	Melting point of			Yield %	Analysis
			Preparation	Picrate	Iodo-methyl-ate		
1	O-Methyl-lupinine		257°	—	—	43.9	4.930 mg. subst.: 0.333 ml. N ₂ (15°, 722 mm) 3.630 mg. subst.: 0.230 ml. N ₂ (15°, 722 mm) Found %: 7.60, 7.68. C ₁₁ H ₂₁ ON. Calculated %: 7.65.
2	O-Ethyl-lupinine		255°	—	274°	60.0	2.820 mg. subst.: 0.175 ml. N ₂ (25°, 721 mm) 3.180 mg. subst.: 0.196 ml. N ₂ (25°, 721 mm) Found %: N 7.65, 8.90. C ₁₂ H ₂₃ ON. Calculated %: N 7.10.
3	O-Propyl-lupinine		61-61	—	262-263	56.2	2.360 mg. subst.: 0.421 ml. N ₂ (25°, 720 mm) 3.990 mg. subst.: 0.245 ml. N ₂ (25°, 720 mm) Found %: N 6.80, 6.67. C ₁₃ H ₂₅ ON. Calculated %: N 6.73.
4	O-Butyl-lupinine		60-61	—	270	50.0	4.330 mg. subst.: 0.220 ml. N ₂ (11°, 719 mm) 4.880 mg. subst.: 0.235 ml. N ₂ (11°, 719 mm) Found %: N 5.78, 6.04. C ₁₄ H ₂₇ ON. Calculated %: N 6.22.
5	O-Phenyl-lupinine		B. p. mm. 190-193 (15 mm)	134-136°	220	36.6	0.529 mg. subst.: 0.255 ml. N ₂ (13°, 727 mm) 3.080 mg. subst.: 0.314 ml. N ₂ (13°, 727 mm) Found %: N 11.54, 11.67. C ₂₀ H ₂₃ O ₂ N. Calculated %: N 11.81.
6	O-Cresyl-lupinine (ortho)		56-58	168-169	232	46.5	4.450 mg. subst.: 0.216 ml. N ₂ (12°, 716 mm) 4.630 mg. subst.: 0.225 ml. N ₂ (12°, 716 mm) Found %: N 5.48, 5.28 C ₁₇ H ₂₁ ON. Calculated %: N 5.40.
7	O-Cresyl-lupinine (para)		53-51	138-140	220-221	34.9	6.450 mg. subst.: 0.324 ml. N ₂ (12°, 718 mm.) 3.230 mg. subst.: 0.160 ml. N ₂ (12°, 718 mm.) Found %: N 5.68, 5.60. C ₁₇ H ₂₁ ON. Calculated %: N 5.40.
8	O-Naphthyl-lupinine (2)		109-110	146-147	243-244	77.8	5.800 mg. subst.: 0.256 ml. N ₂ (20°, 722 mm.) 4.400 mg. subst.: 0.196 ml. N ₂ (20°, 712 mm.) Found %: N 4.82, 4.86 C ₂₀ H ₂₅ ON. Calculated %: N 4.75.
9	Diethylamino-ethanol ether of lupinine		B. p. 130-132 (11 mm)	202-203	195-196	73.9	3.540 mg. subst.: 0.451 ml. N ₂ (15°, 725 mm) 3.150 mg. subst.: 0.385 ml. N ₂ (15°, 725 mm) Found %: N 14.56, 13.85. C ₂₀ H ₃₅ O ₂ N ₂ . Calculated %: N 14.20.

in ordinary organic solvents and sparingly soluble in cold water; stable on storing. The phenyl and diethylaminoethanol ethers are oily liquids. The compounds obtained and the analytical results are given in the accompanying table:

EXPERIMENTAL

O-Butyllupinine

19.1 g. of sodium lupinate was suspended in 60 ml. of n-butyl alcohol. The suspension was heated to 145°C on an oil bath, and 14 g. butyl bromide added. The reaction mixture was then heated for 4 hours at 145°-155°C and filtered while hot. Butyl alcohol was distilled off from the solution in *vacuo*. Residue - thick liquid, which on prolonged standing formed crystals. Recrystallization from acetone gave colorless long yellow-tinted needles, m.p. 60-61°C. Yield 11.2 g. (50%).

The other ethers were synthesized in a similar manner.

Chlorolupinan

Chlorolupinan was synthesized by the method of Bertholomens and Schaumann [6]. 45 g. of lupinine base was dissolved in 200 ml. dry benzene, and to this solution, with efficient stirring, was gradually added 40 g. thionyl chloride. In order to control the reaction, the reaction mixture was cooled with cold water. After adding the total amount of thionyl chloride the mixture was heated on a water bath at a temperature of 50-60°C for 3 hours. After distilling off the benzene the residue was cooled and diluted with a small amount of water, made alkaline with a 50% solution of sodium hydroxide and extracted 3 times with ether; the ether solution was dried over sodium sulfate, and the ether was distilled off. The residue was subjected to vacuum distillation; chlorolupinan distilled over at 127°C (12 mm) as a slightly yellow oil. Yield 45 g. (90.2%).

The picrate, obtained by mixing the alcoholic solutions of the base and picric acid and purified by recrystallization, has a m.p. of 141-143°C.

4.440 mg. substance: 0.515 ml N_2 (11°, 727 mm)

3.447 mg. substance: 0.402 ml N_2 (11°, 727 mm)

Found %: N 13.31; 13.40

$C_{10}H_{15}NO_7 \cdot C_6H_3(OH)(NO_2)_3$. Calculated %: N 13.32.

O-Phenyl-lupinine

A mixture of 9.4 g. chlorolupinan, 4.7 g. phenol and 2 g. potassium hydroxide was placed in a sealed tube and heated for 3 hours at 125-130°C. After cooling, the contents of the tube were dissolved in 50 ml. water and extracted with ether. The ether solution was dried and distilled off. The residue -- a thick oil -- was vacuum distilled. The main fraction distilled over at 190-193°C (15 mm) as a colorless oil. Yield 4.5 g. (86.6%).

Mixing the alcoholic solutions of the base and picric acid yielded the picrate at once. The precipitate was recrystallized from methyl alcohol; shiny crystals formed, m.p. 134-136°C.

The other ethers of the aromatic series were obtained in a similar manner.

CONCLUSIONS

1. Lupinine ethers with the radicals: methyl, ethyl, propyl and butyl have been synthesized using sodium lupinate and alkyl halides.
2. Lupinine ethers with radicals: phenyl, o- and p-cresyl, α -naphthyl and diethylaminoethyl have been synthesized starting with chlorolupinan and the corresponding aromatic hydroxyl-containing compounds and substituted alcohols.
3. All ethers, with the exception of O-phenyl-lupinine and diethylaminoethanol, are crystalline substances. They have been characterized by formation of their picrates and iodomethylates, and by analysis.

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ALKALOIDS OF THE PAPAVERACEAE FAMILY. X. STRUCTURE OF ISOTHEBAINE

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In one of the earlier papers ^[1] the isolation of isothebaine from a wild type of poppy — *Papaver bracteatum*, was reported. The present paper covers the results of the investigation of the structure of isothebaine.

Isothebaine was first discovered by Gadamer and Klee in *Papaver orientale* ^[2,3]. These investigators suggested formula I • not based upon strict proof. As a result of a Hofmann degradation of isothebaine, they obtained after repeated splitting a resinous neutral substance, which was not further characterized. Oxidation of the latter gave a carboxylic acid $C_{13}H_{10}O_5$, which was decarboxylated and yielded a neutral substance, identified by its picrate, m.p. 160°C.

Gadamer and Klee suggested that the obtained substance was identical with the picrate of 3,4,5-trimethoxyphenanthrene, m.p. 167°C ^[4]. The difference in melting points is, according to the investigators, due to impurities present in the product prepared from isothebaine.

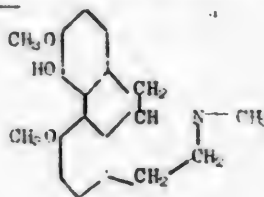
Since we considered the conclusions of Gadamer and Klee as insufficiently substantiated, an investigation was made of the structure of isothebaine, starting with Hofmann degradation, for the following two reasons: first, this would confirm the identity of isothebaine with the substance isolated in this laboratory, and second, a direct comparison could be made of the final product of degradation (VII) with 3,4,5-trimethoxyphenanthrene (IX).

In carrying out a Hofmann degradation the data given by Klee were made more accurate and complete. It has been found that methylation of isothebaine gives good results if the method of Pshorr and Karo ^[5] is used. It was also found that methosulfatemetethylate (II) of isothebaine can be readily converted to iodomethylate by adding a potassium iodide solution to its aqueous solution. Methylation of iodomethylate of isothebaine with dimethylsulfate in alkaline medium, depending on the ratio of the amounts taken of dimethylsulfate and alkali, yields methosulfate or o-methylisothebaine iodomethylate.

In carrying out the first stage of the Hofmann degradation under conditions of Pshorr and Karo, trimethylamine is split off. The substance containing no nitrogen (V) obtained in an insignificant yield, was characterized by its picrate. The reaction proceeds in a similar way with the use of pure crystalline methosulfatemetethylate of isothebaine. When the degradation is carried out by using iodomethylate, no trimethylamine is split off, but a mixture of two desbases is obtained.

Optically inactive des-N-methyl-o-methylisothebaine (III) was isolated as a picrate, which appeared as orange red needles sparingly soluble in alcohol. The picrate of the optically active desbase separates as yellow needles readily soluble in alcohol. The different colors of the picrates greatly facilitated the separation of the isomers.

It is of interest that this reaction with isothebaine iodomethylate results in one optically active substance (X) characterized by its picrate, a crystalline substance of red color.



(I)

The second stage of Hofmann degradation was conducted both with a mixture of two desbases, and with each of them separately. In all cases there was a separation of a large amount of trimethylamine and of the same substance containing no nitrogen (V); the latter was characterized by its picrate -- violet needles.

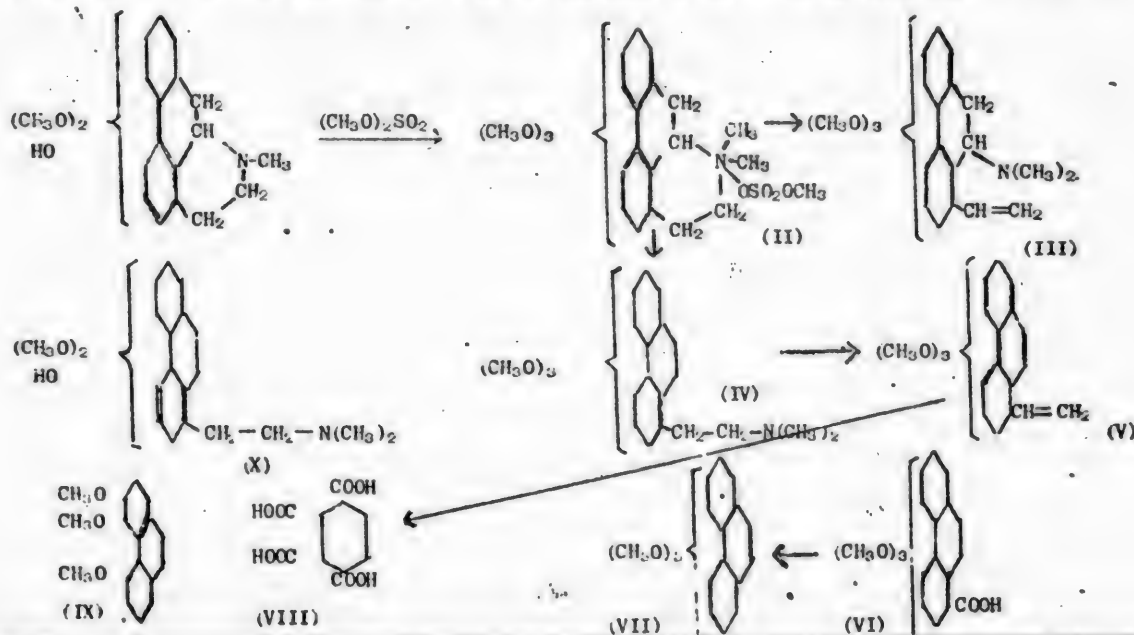
The oxidation of the substance containing no nitrogen yields carboxylic acid (VI), which was decarboxylated in the presence of copper-chromium catalyst^[a]. The product of decarboxylation, $C_{17}H_{16}O_3$ (VII), was characterized by its picrate, which after numerous recrystallizations from methanol and ethyl alcohol melted at 158-159°C, and consisted of dark red needles.

A comparison of the data obtained in the Hofmann degradation with those given by Klee [2], shows a complete identity of the two (see table). This offers definite proof that the alkaloid obtained from *Papaver bracteatum* is identical with isothebaine

Name	Our data m. p.	Data by Klee m. p.
Methoxyisothethylate-o-methylisothebaine..... [α] _D (water)	237 - 238°C +160.5°	237 - 238°C +158.1°
Des-N-methyl-o-methylisothebaine..... [α] _D (ether)	105° -220.1°	104 - 105° -283.9°
Methoxyisomethylate-of inactive des-base.....	196 - 197°	195 - 196°
Phenanthrene carboxylic acid	173°	170 - 171°
Trimethoxyphenanthrene picrate.....	158 - 159°	160°

In a direct comparison of the picrate of the decarboxylation product with the picrate of the 3,4,5-trimethoxyphenanthrene it was found that both substances are identical. Therefore, the structural formula of isothebaine is different from that proposed by Gadamer and Klee. Because of this, we sought confirmation of the existence of a phenanthrene ring in isothebaine. In such cases the oxidation method of Wernat [7] is of general acceptance. In the oxidation of the substance containing no nitrogen (V) obtained by a Hofmann degradation of isothebaine, mellofanic acid (VIII) was isolated, which was converted to tetramethyl ether.

Obtaining mellofanic acid from isothebaine offers final proof of the presence of a phenanthrene nucleus in this alkaloid. On the other hand, the results of acetylation and Hofmann degradation indicate the presence of a tetrahydroisoquinoline ring. This had already been pointed out by Gadamer and Klee [2,3]. Therefore, the view that isothebaine belongs to the aporphine series has been confirmed and the reactions mentioned above may be expressed by the following reactions.



EXPERIMENTAL

Methylation of isothebaine by dimethylsulfate: Methosulfate methylate-o-methylisothebaine (II)

10 g. isothebaine was suspended in 100 ml. water. After addition of 52 ml. of 30% sodium hydroxide the heavy fine crystalline precipitate became amorphous and voluminous. Dimethylsulfate was then added in 2-3 ml. portions. The solution became hot and the precipitate went into solution. After adding 32 ml. dimethylsulfate a clear yellow solution was obtained. On cooling, the methosulfatemethylate ether of isothebaine crystallized in fine needles. The precipitate was washed with absolute alcohol; weight 13.8 g., m.p. 235°C; after one recrystallization, m.p. 236-238°C. The m.p. remained unchanged on repeated crystallizations. Methosulfatemethylate is readily soluble in water and is salted out from aqueous solutions with alkali; it is more sparingly soluble in alcohol than in water, and insoluble in ether. The product shows no colored reaction with ferric chloride. On adding aqueous permanganate to aqueous methosulfate, a white precipitate separates.

Methosulfatemethylate is obtained, also, by the methylation of isothebaine iodomethylate when dimethylsulfate is taken in excess and the amount of alkali is close to the theoretical.

0.1023 g. substance; 15 ml water; $l = 10.05$ cm; $\alpha_D +1.1^\circ$; $[\alpha]_D +160.5^\circ$.

19.785 mg. substance: 9.96 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

21.210 mg. substance: 10.80 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

Found %: OCH_3 26.03, 26.32.

$\text{C}_{20}\text{H}_{23}\text{O}_3\text{N} \cdot (\text{CH}_3\text{O})_2\text{SO}_2$. Calculated %: 4OCH_3 27.49.

o-Methylisothebaine iodomethylate

0.5 g. isothebaine iodomethylate was dissolved in 9.3 ml. 10% NaOH and 10 ml. water. To the solution was added 0.5 g. dimethylsulfate, and the mixture was heated for one hour on a water bath. The hot solution was filtered. Upon cooling, a precipitate formed. The precipitate was soluble in an excess of boiling alcohol. The hot solution was filtered. After evaporating to 10 ml. volume, o-methylisothebaine crystallized in needles which formed rosettes; weight: 0.06 g., melts (with decomposition) at 254°C, after first turning black. After recrystallization from ethyl alcohol, m.p. 256°C (with decomposition). Iodomethylate can be obtained more simply by adding aqueous potassium iodide to aqueous o-methylisothebaine methosulfatemethylate. After mixing both solutions, iodomethylate precipitates as a white powder; from diluted solutions iodomethylate crystallizes in fine white needles. Iodomethylate is sparingly soluble in alcohol, water, and chloroform. In a mixture with isothebaine iodomethylate or with o-methylisothebaine methosulfatemethylate the m.p. shows no depression. It gives no colored reaction with ferric chloride. When aqueous iodomethylate is made alkaline and aqueous permanganate is added, a green color develops; in neutral solution, the color is red.

19.000 mg. substance: 6.98 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

23.900 mg. substance: 3.64 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

Found %: OCH_3 18.99; 18.70

$\text{C}_{20}\text{H}_{23}\text{O}_3\text{N} \cdot \text{CH}_3\text{I}$. Calculated %: 3OCH_3 19.92.

Hofmann degradation of o-methylisothebaine. First stage - a mixture of des-N-methyl-o-methylisothebaine.

5 g. isothebaine was mixed with 25 ml. 26.5% sodium hydroxide. After efficient stirring the isothebaine crystals disappeared giving rise to a voluminous amorphous precipitate. To the mixture was added in three steps 15.6 ml. dimethylsulfate. The solution became hot, with part of the dimethylsulfate remaining undissolved. 25 ml. of sodium hydroxide of the same concentration was added and the solution was heated on a water bath until no further saponification of dimethylsulfate occurred. The reaction was continued without heating, and dimethylsulfate was dissolved completely. The solution was diluted with 160 ml. of water, and 135 ml. sodium hydroxide (26.5%) was added. A yellow oil was collected on the surface of the solution. A separation of trimethylamine was observed. Upon cooling, the alkaline solution was extracted with ether and all the oil was taken into solution. The ether extract was washed several times with 5% sulfuric acid and with water to a neutral reaction and dried over ignited sodium sulfate. After distilling off ether, 0.1 g. resin was obtained: this was slightly soluble in methyl alcohol. The methylalcohol solution was filtered off, and by adding an alcoholic solution of picric acid, a precipitate was formed (fine, dark violet needles, m.p. 129°C). This gave

no depression in the melting point in a mixture with the picrate of the substance containing no nitrogen which was obtained in the second stage of the Hofmann degradation (see below). The acidic solution of the mixture of des-bases was made alkaline by adding 25% ammonia. A white precipitate was formed which was extracted with ether. The ether extract was dried over sodium sulfate, and the ether was distilled off. After removing the ether, 5.1 g. of mixture of des-bases was obtained. The yield, considering the substance containing no nitrogen, is 95.8%.

0.3194 g. substance: 15.1 ml. ether; $n_D^{20} = 1.005$; $\alpha_D - 3.3^\circ$; $[\alpha]_D - 155.5^\circ$.

Then the mixture of des-bases was dissolved in alcohol and an excess of picric acid added to the solution. A mixture of yellow and orange crystals was formed.

Optically active des-N-methyl-o-methylisothebaine (III) was separated readily as a white crystalline powder, when the mixture of des-bases was treated with methyl alcohol. After one recrystallization from methanol, the m.p. was 105°C , and remained unchanged after repeated recrystallization. This substance was readily soluble in ether, more sparingly so in methanol (approximately 1:2 in boiled methanol), insoluble in water, and discolored readily with potassium permanganate. In a slightly acidic solution it gave no colored reaction with ferric chloride. The solution of the base gave an alkaline reaction with litmus.

0.1519 g. substance: 10.5 ml. ether; $n_D^{20} = 1.005$; $\alpha_D - 3.2^\circ$; $[\alpha]_D - 220.1^\circ$.

2.939 mg. substance: 7.994 mg. CO_2 : 1.965 mg. H_2O .

3.523 mg. substance: 9.585 mg. CO_2 : 2.345 mg. H_2O .

3.910 mg. substance: 0.161 ml. N_2 (27°, 724.5 mm)

3.640 mg. substance: 0.148 ml. N_2 (27°, 724.5 mm)

9.550 mg. substance: 25.17 ml. 0.02 M $\text{Na}_2\text{S}_2\text{O}_3$.

8.730 mg. substance: 22.89 ml. 0.02 M $\text{Na}_2\text{S}_2\text{O}_3$.

Found %: C 74.18, 74.20; H 7.46, 7.45; N 4.46, 4.41;

OCH_3 27.25, 27.11.

$\text{C}_{21}\text{H}_{25}\text{O}_3\text{N}$. Calculated %: C 74.34; H 7.35; N 4.13; 3OCH_3 27.43.

The picrate was obtained by mixing the alcoholic solution of des-base and picric acid; it dissolved on heating. On cooling the picrate crystallized in fine yellow needles of m.p. 175°C .

In other experiments using the Hofmann degradation, the following results were obtained: Pure crystalline methacetylcholine (4.6 g.) in aqueous alkaline solution (60 ml. water and 60 ml. 30% sodium hydroxide) gave 3.3 g. mixture of des-bases, $[\alpha]_D - 135.5^\circ$, 0.4202 g. substance: 24 ml. ether; $n_D^{20} = 1.005$; $\alpha_D - 2.4^\circ$. The content of optically active des-base was 61.2%. The liberation of trimethylamine started during the reaction.

o-methylisothebaine iodomethylate (2 g.) with a solution of sodium hydroxide in a mixture of water and alcohol (30 ml. water, 27 ml. 30% sodium hydroxide and 20 ml. alcohol) gave 1.4 g. of a mixture of des-bases $[\alpha]_D - 120.5^\circ$ (0.1090 g. substance: 12 ml. ether; $n_D^{20} = 1.005$; $\alpha_D - 1.1^\circ$). The content of optically active des-base 54.9%. In cases of decomposition with iodomethylate no separation of trimethylamine was noticed. Yields of mixture of des-bases are 95-98% of theoretical.

Separation of mixture of des-bases. When 4.39 g. of the mixture was treated with methanol, there was a partial separation of the optically active des-base. The residue in the mother liquor weighed 2.4 g. It was dissolved in an excess of methyl alcohol, and to the solution an alcoholic solution of picric acid was slowly added. First an orange colored picrate precipitated; this was filtered under suction as soon as this light-colored precipitate appeared. The orange picrate weighed 2.46 g., m.p. $201-202^\circ\text{C}$. After further addition of picric acid to the mother liquor, 1.23 g. of yellow powder of m.p. 174°C formed; this substance was found to be the picrate of the optically active des-base.

The picrate of the optically inactive des N-methyl-o-methylisothebaine (IV). The orange precipitate, weighing 2.46 g., m.p. $201-202^\circ\text{C}$, was treated with 125 ml. of boiling alcohol; part of the substance was soluble, the insoluble residue weighed 1.8 g., m.p. $201-202^\circ\text{C}$. 0.5 g. of this substance was recrystallized from a mixture of 15 ml. absolute alcohol and 100 ml. ethyl acetate. Yield 0.2 g. of fine orange-red needles, m.p. 202°C . The color of this picrate resembled that of the picrate of des-N-methylisothebaine. The mixture of both picrates gave a depression of the melting point. The picrate of the optically inactive des-base is sparingly soluble in methanol, ethyl alcohol, and ethyl acetate.

3.885 mg. substance: 0.345 ml. N_2 (17°, 742 mm).
 3.865 mg. substance: 0.341 ml. N_2 (17°, 742 mm).
 Found %: N 10.20, 10.14.

$C_{21}H_{25}O_3N \cdot C_6H_5O_2N_3$. Calculated %: N 9.86.

Methosulfatemethylate of optically inactive des-N-methylisothebaine. 0.17 g. base, obtained by the decomposition of picrate (m.p. 202°C) was dissolved in 30-40 ml. ether. To the solution was added a large excess of dimethylsulfate (3ml.). The entire mixture became turbid very rapidly, and no longer remained alkaline. When allowed to settle for a long time (10-12 hours) a white precipitate was collected on the bottom and the mother liquor became clear. After decantation, the residue was worked with ether and treated with 5-6 ml. methyl alcohol. A white crystalline substance, m.p. 196-197°C, precipitated. After recrystallization from methyl alcohol, methosulfatemethylate was obtained in fine white needles of the same melting point. For the treatment of mother liquor, see below.

Preparation of the substance containing no nitrogen (V). To a solution of 5.1 g. of a mixture of des-bases in 65 ml. ether was added in two steps 4 ml. dimethylsulfate. A white turbidity appeared which settled on standing for 4½ hours. This was converted to a resin, including separate crystals. The ethereal mother liquor was decanted, and the residue washed with ether. After being allowed to stand, another 0.9 g. of material precipitated from the ether. Total amount of the mixture of methosulfatemethylates 8.0 g; the mixture was dissolved in 75 ml. of methyl alcohol. To the solution was added 18.9 g. potassium hydroxide and the mixture was boiled for 3 hours. Trimethylamine precipitated in a large amount; a white precipitate was gradually formed. Methyl alcohol was distilled off, the residue was dissolved in 150 ml. water an insignificant amount remaining undissolved. The mixture was extracted with ether until a drop of the ether extract, when mixed with a small amount of an alcoholic solution of picric acid, gave no additional violet precipitate. The ether extract was washed with 5% sulfuric acid to a complete extraction of the bases, and then with water and dried over potassium carbonate. The residue after removal of ether weighed 4.05 g., 79.9% of theoretical, based on the mixture of desbases, or 76.8% based on isothebaine. The acidic wash waters were extracted with ether after having been made alkaline with ammonia. The ether was distilled off. Weight of residue 0.07 g., when treated with methanol turns to a powder of m.p. 102°C, giving no depression in the melting point in a mixture with optically active des-base.

The substance containing no nitrogen is readily soluble in ether, more sparingly in acetone, methyl and ethyl alcohols, and insoluble in water. When stored it forms a white powdery substance, sparingly soluble in methyl and ethyl alcohols and more readily soluble in ether. This substance darkens and softens at 215-219°C; it is also obtained in a Hofmann degradation of des-bases. Attempts to obtain the substance containing no nitrogen in a crystalline state failed.

Picrate of the substance containing no nitrogen. Mixing the alcoholic solutions of the substance containing no nitrogen and picric acid gave a picrate -- violet needles of m.p. 129-130°C.

13.55 mg. substance 23.16 ml. 0.02N. $Na_2S_2O_3$.
 25.90 mg. substance: 44.06 ml. 0.02N. $Na_2S_2O_3$.
 Found %: OCH_3 17.67, 17.59.

$C_{19}H_{19}O_3 \cdot C_6H_5O_2N_3$. Calculated %: $3OCH_3$ 17.76.

Preparation of substance containing no nitrogen (V) from optically active des-base (III). 0.35 g. of des-base was dissolved in 50 ml. ether. An excess of dimethylsulfate was added to the solution. On standing, the solution did not remain alkaline. To the solution was added 75 ml. methyl alcohol, and gradually an excess of ground sodium hydroxide. The mixture was boiled for 2 hours, and the solvents distilled off in vacuo. The residue was treated with 50 ml. water, and the mixture extracted with ether. The ether contained no bases, and after washing with water and drying over sulfate, was distilled off. The obtained resin was dissolved in methyl alcohol and filtered off from the insoluble white powder. To the solution of the substance containing no nitrogen an alcoholic solution of picric acid was added, a dark violet picrate of m.p. 130°C was formed which gave no depression in the melting point with the picrate of the substance containing no nitrogen, described earlier.

Preparation of the substance containing no nitrogen from the optically inactive desbase (IV).

The residue from the mother liquors after separation of the methosulfatemethylate of the optically inactive des-N-methyl-*o*-methylisothebaine was dissolved in methyl alcohol. To the solution was added

0.5 g. sodium hydroxide, and the mixture was boiled for 3½ hours. The methyl alcohol was distilled off in vacuo, the residue treated with 20 ml. water, and the alkaline solution extracted with ether. The subsequent treatment was the same as in the earlier experiments. M.p. of picrate 129°C, gave no depression in a mixture with the picrate of the previous experiment (m.p. of mixture 130°C).

Oxidation of the substance containing no nitrogen with permanganate

Trimethoxyphenanthrene carboxylic acid (VI). 4.05 g. of the substance containing no nitrogen was dissolved in 100 ml. acetone. The solution was filtered off from a white, granular precipitate, weighing 0.1 g.. To the solution was added powdered potassium permanganate to a stable pink coloration. The addition of permanganate was continued for 3 hours at a temperature of 18-20°C. Amount of permanganate used: 9.45 g. Several milliliters of methyl alcohol was added to discolor the solution. Manganese dioxide was filtered off under suction and washed with hot water until the wash water gave no precipitate on acidification. The wash waters were made alkaline, the residue obtained ~~was added~~ and the mixture washed with ether. The ether solution was dried over sodium sulfate. After distilling off the ether there was obtained 0.17 g. of a yellow neutral resin. The alkaline solution was acidified with 5% hydrochloric acid and extracted with ether. The ether extract was dried over sodium sulfate. After distilling off the ether there was obtained 3.4 g. of a brown resin including clusters of crystals. Treating this with alcohol gave a yellow crystalline substance, weighing 1.92 g., m.p. 171-172°C. Another 0.12 g. of a substance of a lower m.p. was obtained from the mother liquor. After recrystallization from alcohol in the presence of carbon black, trimethoxyphenanthrene carboxylic acid, m.p. 173°C, was obtained. On further crystallizations the melting point remained unchanged. Trimethoxyphenanthrenecarboxylic acid was readily soluble in ether and chloroform, and sparingly soluble in water, methanol, and ethyl alcohol. The solutions were acidic to litmus, and slightly acidic to congo red.

2.844 mg. substance:	7.238 mg. CO ₂ :	1.340 mg. H ₂ O.
3.550 mg. substance:	9.050 mg. CO ₂ :	1.590 mg. H ₂ O.
15.375 mg. substance:	8.52 ml. 0.1 N Na ₂ S ₂ O ₃ .	
8.085 mg. substance:	4.52 ml. 0.1 N Na ₂ S ₂ O ₃ .	
Found %:	C 69.41, 69.53;	H 5.27, 5.01; OCH ₃ 28.65, 28.90.
C ₁₆ H ₁₀ O ₅ . Calculated %:	C 69.23;	H 5.13; OCH ₃ 29.88.

The picrate of trimethoxyphenanthrenecarboxylic acid was obtained by adding to the alcoholic solution of the acid an alcoholic solution of picric acid. m.p. of picrate 153°C; after recrystallization from alcohol, m.p. 154°C. The picrate of trimethoxyphenanthrenecarboxylic acid appeared as red needles, readily soluble in methanol, ethyl alcohol, acetone, benzene, petroleum ether, and ethyl acetate.

Trimethoxyphenanthrene (VII). 1.45 g. of trimethoxyphenanthrenecarboxylic acid was dissolved in 20 ml. quinoline, and 4.5 g. copper-chromium catalyst added to the solution. The evolution of carbon dioxide stopped on the completion of boiling. Upon cooling the mixture was diluted with ether and filtered under suction. The ether extract was washed with acid, 10% sodium hydroxide solution, water, and dried over potassium carbonate. After distilling off ether, 1.04 g. of a dark resin was obtained, almost completely soluble in 20-25 ml. alcohol. The admixture remained undissolved even when the solution was boiled. After filtration, an alcoholic solution of picric acid was added to the solution. With the addition of picric acid, the trimethoxyphenanthrene picrate precipitated, weight 1.39 g., m.p. 155-156°C; after two recrystallizations from alcohol, m.p. 157-158°C; 0.88 g. of this substance was suspended in 5-10 ml. water, the mixture made alkaline with ammonia and extracted with ether. The ether extract was washed with alkali. The washing was stopped when no color developed on addition of alkali. After washing with water to a neutral reaction, the ether extract was dried over ignited sodium sulfate, and the ether was distilled off; a resinous substance was obtained. Attempts to obtain a crystalline substance failed. Trimethoxyphenanthrene is readily soluble in ether, sparingly so in methyl and ethyl alcohols.

Trimethoxyphenanthrene picrate. To the alcoholic solution of trimethoxyphenanthrene was added an excess of an alcoholic solution of picric acid. A crystalline picrate, dark red needles, was formed, m.p. 158-159°C; after recrystallizations from methyl or ethyl alcohol, the m.p. remained unchanged. The solubility of the picrate in ethyl alcohol is about 1:15; in methyl alcohol, about 1:35. The

(after evaporation of acetone mother liquor)

picrate is decomposed in water, forming a yellow solution and an amorphous precipitate.

The picrate was compared with the picrate of 3,4,5-trimethoxyphenanthrene, prepared from morphenol and having a m.p. of 163-164°C, softening at 160-161°C. The mixture of both picrates melted at 142-145°C.

15.70 mg. substance:	5.55 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.
14.18 mg. substance:	4.94 ml. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.
Found %:	OCH_3 18.28, 18.01.
$\text{C}_{17}\text{H}_{21}\text{O}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$. Calculated %:	3POCH_3 18.67.

Mellofanic acid (VIII) 2.88 g. of the substance containing no nitrogen was treated with 20 ml. nitric acid (d 1.37). The nitric acid was concentrated; such treatment was repeated 3 times more; then the residue was dissolved with heating in 10 ml. nitric acid. On standing 0.20 g. of yellow crystalline substance of m.p. 230-231°C precipitated. Mellofanic acid, obtained under the same conditions from thebenin, had a m.p. of 233-234°C. A mixture of both substances melted at 232-233°C. Mellofanic acid was methylated by using diazomethane. Its ester, m.p. 131-132°C. The ester of mellofanic acid, obtained from thebenin, melted at 131-132°C. The mixture of both substances melted at the same temperature.

Hofmann degradation of isothebaine.

Des-N-Methylisothebaine(X). To a mixture of 6 g. powdered sodium hydroxide and 25 ml. methyl alcohol was added 2 g. isothebaine iodomethylate. The mixture was boiled for 3 hours. Upon completion of boiling, all the precipitate was in solution. The methyl alcohol solution was concentrated, the residue was dissolved in 20 ml. water, and the alkaline solution was extracted with ether. The ether extract was washed with water and dried over ignited sodium sulfate. After distilling off the ether, 1.2 g. of a brown resin remained; this resin was readily soluble in alcohol and acetone. Sparingly soluble in ether and insoluble in petroleum ether (B.p. 28-30°C) and in water. Des-base is optically inactive (0.1153 g. in 10 ml. hot alcohol, $l = 1.0$ dm., $\alpha = 0$).

The picrate of desbase. To the alcoholic solution of 0.1 des-base was added an excess of an alcoholic solution of picric acid. A brown-red precipitate - 0.2 g., m.p. 198°C, was formed. The picrate was recrystallized from dry acetone. Upon cooling the solution, together with the red picrate crystals, an amorphous, clear precipitate was found which was removed with the mother liquor on decantation. The picrate was treated with 2-3 ml of absolute alcohol and filtered under suction. Weight of picrate 0.05 g., m.p. 206-207°C with softening for 2-3°.

Iodomethylate of des-base. 1.1 g. des-base was dissolved in 5 ml. acetone, and 0.8 ml. of methyl iodide added to the solution. A resin separated at once which was dissolved after adding 25 ml. acetone. Another 0.2 g. methyl iodide was added. The solution was boiled for 2 hours and concentrated to a volume of 10-12 ml. After cooling, a precipitate formed, weighing 1.1 g. Recrystallization from alcohol yielded 1 g. of crystalline iodomethylate. Crystals -- yellow, fine needles, softening at 140-145°C and flowing freely at 145-153°C. Iodomethylate is unstable; darkens on drying (60-80°C) and has a strong odor of trimethylamine.

Substance containing no nitrogen (XI)

In carrying out the second stage of the Hofmann degradation trimethylamine was split off, 0.4 g. resin was separated. The latter was partially soluble in 10% sodium hydroxide. Attempts to purify the resin failed.

CONCLUSIONS

1- In carrying out the Hofmann degradation, additional data have been obtained. Principally the following were found:

- a) the methylation of isothebaine by using dimethyl sulfate takes place under the conditions of Pshorr and Karo;
- b) the first stage of the Hofmann degradation takes place abnormally, i.e., with splitting off of trimethylamine;
- c) des-bases have been separated;
- d) the substance containing no nitrogen has been characterized.

2. It has been shown that the previously reported distribution of substituents in isothebaine is erroneous.

3. The presence of a phenanthrene nucleus in isothebaine has been confirmed by the preparation of mellofanic acid.

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INVESTIGATIONS OF FORMIC ACID SYSTEMS

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In addition to a study of the density, viscosity and electrical conductivity of the systems formic acid - nitrobenzene, formic acid - acetic acid, formic acid - formic ethyl ester and formic acid - ethyl ether [1,2], a study has been made of these systems by the method of molecular weight. [3,4].

Benzene of m.p. 5.5°C was used as a cryoscopic solvent. The determination of the molecular weight was carried out in Beckmann's apparatus [5].

System formic acid - nitrobenzene. The results of the experimental determination of the molecular weight of the formic acid - nitrobenzene system are given in Table 1. From the data given in Table 1 the values of the molecular weight of the dissolved substances, corresponding to 0.0, 0.5, 1.0 and 1.5 g-mol. per 1000 g. benzene can be determined graphically. These values were used for plotting a molecular weight - composition diagram as shown in Fig. 1. On the diagram in Fig. 1 the isoconcentrate I up to 80 mol.% of formic acid is linear, and then becomes convex approaching the composition axis. The isoconcentrate II is almost linear, and the isoconcentrates III and IV linear up to 80 mol. % acid, then concave approaching the composition axis.

System formic acid - acetic acid. The results of measurements of the molecular weight of the formic acid-acetic acid system are given in Table 2. The molecular weight diagram of this system, plotted on the basis of the molecular weight values determined graphically is given in Fig. 2. All isoconcentrates in Fig. 2 are linear.

System formic acid - formic ethyl ester is given in Table 3. The molecular weight diagram of this system is given in Fig. 3. All isoconcentrates pass through a maximum, shifted towards formic acid.

System formic acid - ethyl ether. In table 4 are given the results of measurements of molecular weight of formic acid - ethyl ether system. On the basis of the molecular weight values determined graphically a diagram was plotted as shown in Fig. 4, where all the isoconcentrates pass through a maximum, shifting towards formic acid. In the preparation of the formic acid - ethyl ether mixture a positive thermal effect was observed.

DISCUSSION OF RESULTS

In the formic acid - nitrobenzene system the isoconcentrates in the molecular weight diagram (Fig. 1), exhibit a complex trend; here a curve can be observed, convex approaching the composition axis, linear for the isoconcentrate, and, finally, concave approaching the abscissa. In the high concentration of nitrobenzene region, the curves straighten out. In an examination of the data on viscosity and electrical conductivity [1] it was pointed out that there was a chemical reaction between the molecules of formic acid and nitrobenzene. The chemical behavior of the system and the dissociation of the associated components can be judged from the molecular weight diagram. When nitrobenzene is added to formic acid, then, depending upon the amount of the mixture in benzene the interaction of the components and the dissociation of associated molecules exert varying influences. In strong dilutions the molecules are associated less, therefore the reaction between the components exerts a greater influence, and the isoconcentrates

Table 1
Formic acid - nitrobenzene

HCOOH (Mol.%)	Number of moles of substance in 1000 g benzene	Δt	M	HCOOH (Mol.%)	Number of moles of substance in 1000 g. benzene	Δt	M
0.00	0.1067	0.550	121.2	68.93	0.1491	0.518	102.3
	0.2847	1.151	126.2		0.3791	1.249	106.6
	0.3626	1.735	123.2		0.6540	2.059	110.2
	0.5759	2.680	129.9		0.9024	2.739	113.1
	0.6500	3.009	129.9		1.1414	3.340	116.2
	0.8659	3.852	133.3		1.4751	4.155	119.1
10.24	0.1480	0.719	119.9	76.79	0.1392	0.445	99.3
	0.2432	1.358	124.6		0.4455	1.340	104.0
	0.4400	1.982	126.9		0.7579	2.188	108.9
	0.5998	2.643	128.3		1.2390	3.323	113.0
	0.7613	3.274	130.2		1.5283	3.944	116.3
	1.0195	4.242	132.5		0.2120	0.627	99.6
17.91	0.1414	0.659	118.8	84.33	0.4393	1.232	104.1
	0.3817	1.670	123.9		0.6881	1.863	106.8
	0.6306	2.674	126.5		1.1078	2.770	113.9
	0.8737	3.591	128.7		0.2317	0.648	98.3
	1.1010	4.387	131.0		0.5003	1.319	103.2
					0.8263	2.055	106.1
26.91	0.1426	0.634	116.7	93.80	1.2706	3.025	111.2
	0.3023	1.301	119.3		1.7810	3.894	119.5
	0.4550	1.910	121.9		0.2768	0.743	95.8
	0.6138	2.530	122.2		0.5351	1.561	103.3
	0.8389	3.320	125.7		0.9062	2.149	106.1
					1.2273	2.740	111.6
	0.1684	0.730	110.9	100.0	1.5694	3.197	121.5
	0.3580	1.450	117.2		0.1020	0.279	85.6
	0.5404	2.138	118.7		0.2758	0.710	91.7
	0.6991	2.707	120.2		0.4339	1.055	95.4
	0.8577	3.237	122.3		0.6969	1.592	100.6
					0.9581	2.074	105.4
52.29	0.1649	0.640	108.4		1.4112	2.784	114.4
	0.3280	1.224	111.4				
	0.5624	2.011	114.9				
	0.7712	2.681	116.9				
	1.0786	3.580	120.7				
	1.2062	3.941	121.9				

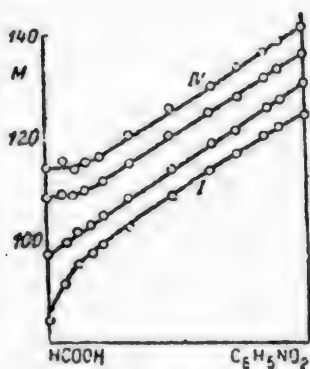


Fig. 1

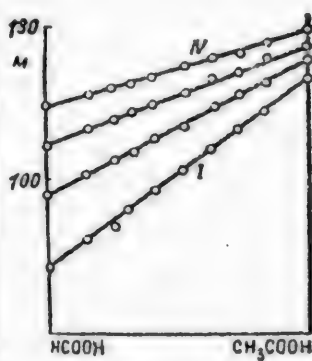


Fig. 2

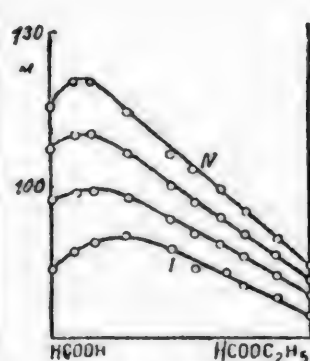


Fig. 3



Fig. 4.

Table 2

Formic acid - acetic acid

HCOOH (mol%)	Number of moles of substance in 1000 g. benzene	Δt	M	HCOOH (mol%)	Number of moles of substance in 1000 g. benzene	Δt	M
0.00	0.0376	0.097	118.8	60.09	0.0983	0.270	95.8
	0.2583	0.650	120.9		0.2326	0.594	102.6
	0.4977	1.213	123.8		0.4494	1.097	106.4
	0.9720	2.300	125.1		0.5316	1.488	109.6
	1.6320	3.659	129.4		0.8924	2.020	113.1
16.99	0.1298	0.239	112.4	67.58	1.1587	2.536	116.6
	0.2028	0.610	115.7		0.0745	0.202	95.9
	0.3907	0.989	116.8		0.1988	0.519	99.8
	0.5574	1.331	121.1		0.4232	1.028	104.9
	0.7853	1.832	123.9		0.6370	1.485	108.5
27.32	1.0139	2.314	124.7	75.10	1.0110	2.234	113.2
	0.0813	0.208	112.3		0.1204	0.319	95.2
	0.2712	0.695	111.1		0.3173	0.793	100.2
	0.5463	1.325	116.3		0.5339	1.273	104.3
	0.7398	1.755	118.1		0.7237	1.772	109.1
37.16	0.9037	2.115	118.9	84.35	1.2110	2.575	114.5
	1.0976	2.469	121.6		1.3615	2.831	117.1
	0.0718	0.191	105.2		0.1205	0.316	93.7
	0.2165	0.540	111.6		0.3739	0.918	99.1
	0.4383	1.058	114.4		0.6231	1.461	103.9
49.27	0.6133	1.458	115.4	100.00	0.8504	1.906	106.5
	0.8594	1.980	118.2		1.1696	2.494	111.4
	1.0710	2.410	120.1		1.4115	2.894	115.0
	0.0748	0.195	104.0		0.1020	0.279	85.6
	0.3445	0.865	106.9		0.2758	0.701	91.7
	0.6144	1.465	111.5		0.4339	1.155	95.4
	0.9886	2.250	115.4		0.6969	1.592	100.6
	1.2955	2.815	119.8		0.9581	2.074	105.4
					1.4112	2.784	114.4

are concave approaching the composition axis. The linear course of isoconcentrates may be due to the mutually compensating effect of the dissociation of the associated molecules of the components and that of their interaction.

Thus, the complex character of the isoconcentrates of molecular weight is in full accord with the isotherms of viscosity and electrical conductivity [1,2]. This is believed due to the chemical interaction of the components.

In the formic acid - acetic acid system the isoconcentrates are linear (Fig. 2). The components of this system are associated; when mixed, dissociation of associated molecules, as well as chemical interaction, takes place. The process of dissociation of associated molecules results in a decrease of the apparent molecular weight, and chemical interaction results in an increase. The superposition of these two effects acting in opposite direction is apparently the cause for the additive summation of the apparent molecular weight. The existence of a reaction between the molecules of formic and acetic acids is confirmed by the data on viscosity [3]; whereas, the diagram of electrical conductivity, being concave approaching the composition axis, exhibits a monotonous drop along its whole length [1], without any reflection of the interaction.

Table 3
Formic acid - formic ethyl ester

HCOOH (mol %)	Number of moles of substance in 1000 g. benzene	Δt	M	HCOOH (mol %)	Number of moles of substance in 1000 g. benzene	Δt	M
0.00	0.0881	0.434	76.5	56.03	0.1411	0.480	87.2
	0.1595	0.783	76.3		0.3512	1.127	91.5
	0.2495	1.219	76.2		0.5705	1.740	95.4
	0.3591	1.714	77.4		0.8351	2.457	97.7
	0.4388	2.077	77.6		1.1690	3.258	101.9
	0.5926	2.721	79.1		1.4923	3.950	106.1
	0.5008	2.351	77.9	70.06	0.1728	0.496	95.9
14.25	0.0888	0.394	80.7		0.3766	1.061	96.8
	0.2386	1.097	81.6		0.6005	1.628	100.0
	0.5935	2.450	84.0		0.8128	2.123	102.7
	0.7604	3.090	84.5		1.0675	2.653	107.1
	0.9409	3.720	85.0		1.4381	3.353	112.9
26.97	0.1157	0.485	80.7	84.30	0.1518	0.429	90.8
	0.2564	1.025	83.9		0.4434	1.136	99.9
	0.4508	1.745	85.6		0.7318	1.757	104.6
	0.6567	2.480	86.7		1.0141	2.288	110.4
	0.9692	3.504	89.1		1.3846	2.855	117.2
33.57	0.1157	0.412	84.3	91.05	0.1736	0.462	92.7
	0.2406	0.911	86.2		0.4857	1.202	98.6
	0.3858	1.417	88.2		0.7508	1.740	104.4
	0.5170	1.850	89.8		0.9625	2.127	108.8
	0.7602	2.631	91.8		1.4066	2.797	119.6
45.80	0.9500	3.200	93.5	100.00	0.1020	0.279	85.6
	0.1550	0.561	85.9		0.2759	0.701	91.7
	0.2960	1.043	87.5		0.4339	1.055	95.4
	0.4857	1.633	90.9		0.6969	1.592	100.6
	0.6588	2.128	98.9		0.9581	2.074	105.4
	0.8637	2.708	95.8		1.4112	2.784	114.4
	1.1875	3.380	98.7				

In the formic acid-formic ethyl ester and formic acid-ethyl ether systems (Figs 3 and 4) all isoconcentration diagrams of molecular weight pass through a maximum, shifting toward formic acid. This type of shape of isoconcentrates in systems with associated components indicates a considerable interaction between the components. The shifting of the maximum of molecular weight curves is possibly a result of the interaction of formic acid. The composition of the compounds which are formed becomes more complex with an increase in the concentration of the acid.

The processes taking place in the systems formic acid - formic ethyl ester and formic acid - ethyl ether appear differently on the diagrams of the various properties.

In the system formic acid - formic ethyl ester, the viscosity curves $[\eta]$ are concave approaching the composition axis and, therefore, they reflect only the dissociation of the associated molecules of the components. The diagrams of molecular weight (Fig. 3) and electrical conductivity $[\kappa]$ indicate the existence of chemical interaction. In the system formic acid - ethyl ether, the formation of the compound could not be detected either from viscosity isotherms $[\eta]$ or from the isotherms of electrical conductivity $[\kappa]$. The presence of inter-

Table 4

Formic acid - ethyl ether

HCOOH (Mol.%)	Number of moles of substance in 1000 g. benzene	Δt	η	HCOOH (Mol.%)	Number of moles of substance in 1000 g. benzene	Δt	η
0.00	0.0623	0.300	78.3		0.6304	1.985	103.8
	0.1698	0.806	78.9		0.8475	2.643	107.3
	0.2422	1.142	79.1		1.2049	3.360	110.8
	0.3022	1.418	79.1				
	0.4284	2.013	78.2	69.60	0.1708	0.495	95.7
	0.5930	2.755	78.2		0.4378	1.186	101.2
	0.7841	3.623	77.6		0.8490	2.108	108.9
	0.8790	3.913	77.9		1.0869	2.593	112.4
15.69					1.3478	3.090	116.1
	0.1618	0.666	85.8	76.67	0.2129	0.588	96.5
	0.3387	1.367	86.5		0.4679	1.185	104.4
	0.5233	2.115	85.4		0.6752	1.811	108.5
	0.7038	2.811	85.5		0.9984	2.320	111.8
25.29	0.9079	3.550	86.3		1.2825	2.840	116.3
					1.6700	3.502	121.5
	0.1225	0.470	88.7				
	0.2824	1.067	89.3	86.45	0.3047	0.773	97.7
	0.5521	2.032	90.3		0.6739	1.561	105.7
	0.6718	2.449	90.5		0.9703	2.139	110.0
37.02	0.7869	2.830	91.2		1.3889	2.849	116.0
	0.9661	3.419	91.0		2.0231	3.735	128.1
				100.00	0.1020	0.279	85.6
	0.1847	0.653	91.3		0.2758	0.701	91.7
	0.3954	1.348	93.7		0.4339	1.055	95.4
50.67	0.6540	2.148	96.0		0.6969	1.592	100.6
	0.9388	2.998	97.4		0.9581	2.074	105.4
	1.1261	3.514	98.9				
					1.4112	2.784	114.4
	0.1861	0.538	93.6				
	0.3990	1.182	99.3				

action between formic acid and ethyl ether is clearly indicated by the distinctly expressed maximum on the isoconcentrates of molecular weight (Fig. 4) and by the positive thermal effect of mixing.

Thus, a comparison of the diagrams of viscosity, electrical conductivity [1,2] and molecular weight indicates that individual properties do not reflect to the same extent the peculiarities of the system and give no simple presentation. In the formic acid - acetic acid system, from the shape of the viscosity [1] and molecular weight (Fig. 2) diagrams a reaction between the components occurs; from the course of electrical conductivity isotherms, [1], no statement can be made about the presence of such an interaction.

From the molecular weight (Fig. 3) and electrical conductivity [2] diagrams of the formic acid - formic ethyl ester systems the presence of an interaction between the components can be pointed out, which is not reflected in the viscosity isotherms [2].

And, finally, in the formic acid - ethyl ether system the maximum of the molecular weight diagram confirms the existence of a considerable interaction between the components (Fig. 4). Whereas, neither from the viscosity [2] nor electroconductivity [2] isotherms can such a statement be made. The reasons for the deviations exhibited by the curves can be explained as follows.

The electrical conductivity isotherms of the formic acid - acetic acid [1] and the formic acid - ethyl ether [2] systems are concave approaching the composition axis. The possibilities of the presence of such isotherms was originally established by M.I. Usanovich [7]. In a study of the systems with components which form no chemical compounds, M.I. Usanovich obtained curves convex toward the composition axis. Taking this as a basis, M.I. Usanovich considers that the electrical conductivity isotherms being concave approaching the abscissa indicates the absence of any interaction between components. However, such a shape of the electrical conductivity isotherms can be also explained as a result of the interaction of the components forming a non ionic compound. As an example of such a case -- the formic acid - acetic acid and formic acid - formic ethyl ester systems.

As far as the deviations exhibited by the viscosity and molecular weight curves, it is known that the viscosity isotherms are concave approaching the abscissa. This is not in contradiction with the statement on the presence of chemical interaction in the system.

CONCLUSIONS

1. By using the molecular weight method the following systems have been investigated: formic acid - nitrobenzene, formic acid - acetic acid, formic acid - formic ethyl ester, and formic acid - ethyl ether.
2. A comparison has been made of the molecular weight method with the viscosity and electrical conductivity methods.

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VISCOSITY RELATIONSHIPS OF CHLORAL SYSTEMS WITH ALCOHOLS

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The viscosity isotherms of binary liquid systems, depending on the nature of the reaction between the components, can be either regular or irregular. The regular isotherms are those whose maximum corresponds exactly to the composition of the compound formed, and the maximum is not shifted on the concentration axis with a change in temperature. The irregular isotherms have a maximum which does not correspond to a regular ratio of the components, and with a rise in temperature, as a rule, according to N. S. Kurnakov, the maximum is shifted towards the more viscous component. Such a shifting of the maximum toward the more viscous component or even its disappearance on the viscosity isotherms is explained by N. S. Kurnakov as due to a partial or even complete dissociation of the compound found in the liquid phase above its melting point [1,2,3]. Thus, N.S. Kurnakov and N.N. Efremov [1] in an investigation of the chloral—water and chloral—ethyl alcohol systems, believe that the shifting of the maximum of the viscosity isotherms of these systems is due to the dissociation of chloral-hydrate or chloral-alcoholate.

However, such an explanation is not in full agreement with the known experimental facts. In fact, the maximum on the viscosity isotherms of these systems is not shifted toward the more viscous component - chloral, but rather toward the less viscous component. Moreover, the compounds formed, chloral hydrate and chloral-ethylalcoholate, are stable compounds and do not dissociate into any components, as may be confirmed from a cryoscopic determination of their molecular weights [4,5]. Consequently, there are irregular systems, in which the shifting of the maximum on the viscosity isotherms can not be interpreted as due to a dissociation of compounds formed. V.V. Udovenko [6] was the first to point this out. He showed that the irregular maximum may appear also where a stable compound is formed which will react further with one of the components in the system. In this case, independent of the magnitude of the viscosity, the irregular maximum would be shifted toward that component with which the resulting stable chemical compound would react.

The object of the present investigation is to develop this interpretation of V.V. Udovenko. For this purpose, those systems were chosen in which the components formed stable compounds, i.e. systems of chlorals and fatty alcohols. In these systems, as shown, by cryoscopic investigations, the chloral-alcoholates react with the alcohols, and therefore the irregular maximum should be shifted towards the alcohol, independent of the viscosity value. For the alcohols, methyl and isoamyl (inactive) alcohols were taken, since the viscosity of the first was considerably less and the second considerably greater than the viscosity of chloral.

The chloral was prepared from chloral hydrate by the method described by Liebig, in which concentrated acid was used as a degrading agent. The chloral obtained was distilled over freshly ignited lime. The fraction boiling at 96.5°C and 726 mm pressure was collected and distilled directly into ampules in a distilling apparatus, as described in the paper by M. Usanovich, T. Samarokova and V. Udovenko [6].

Molecular % of chloral	40°		60°		75°	
	d	η	d	η	d	η
0.00	0.7751	0.4555	0.7491	0.3458	—	—
3.65	0.8891	0.5111	0.8412	0.3332	—	—
11.52	1.1100	0.9078	0.9904	0.6707	—	—
24.68	1.2356	2.0962	1.2015	1.3973	1.1812	1.0505
30.32	1.3130	2.4913	1.2830	1.6507	1.2380	1.2065
42.07	1.4278	6.0854	1.4009	2.8870	1.3845	1.3685
44.40	1.4462	5.5908	1.4201	3.2436	1.3878	1.9456
47.31	1.4635	7.3837	1.4680	3.2830	1.3946	1.9416
50.32	1.4838	7.0280	1.4421	3.1392	1.4114	1.9154
59.58	1.4932	3.1817	1.4690	1.7936	1.4295	1.3788
71.59	1.5102	1.7920	1.4691	1.2052	1.4333	0.9753
84.16	1.5046	1.1980	1.4513	0.9218	1.4335	0.7225
96.03	1.4903	0.8738	1.4531	0.6813	1.4304	0.5685
100.00	1.4795	0.8411	1.4458	0.6511	1.4060	0.5539

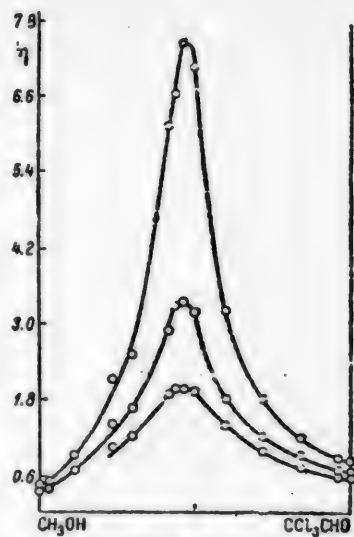


Fig. 1

molecular % of chloral	40°		60°		80°	
	d	η	d	η	d	η
0.00	0.8003	2.3761	0.7836	1.4300	0.7665	0.8834
7.15	0.8582	2.8249	0.8377	1.6501	0.8207	1.0230
22.26	0.9804	4.0980	0.9661	2.2335	0.9452	1.3408
28.51	1.0402	4.6839	1.0256	2.4667	1.0076	1.4484
35.09	1.0907	5.4761	1.0693	2.8069	1.0515	1.6567
40.01	1.1416	6.0696	1.1211	3.0140	1.0958	1.8013
43.35	1.1796	6.4802	1.1446	3.1042	1.1211	1.8607
45.73	1.1922	6.9230	1.1676	3.1210	1.1428	1.8449
47.22	1.2076	6.9223	1.1847	3.2835	1.1553	1.8285
48.23	1.2105	6.8309	1.1855	3.0906	1.1572	1.8047
49.26	1.2184	6.7507	1.1947	3.1470	1.1661	1.8054
52.51	1.2441	6.0251	1.2184	2.9723	1.1943	1.7591
55.76	1.2628	5.4056	1.2364	2.7677	1.2130	1.6535
61.65	1.2957	3.9351	1.2721	2.3512	1.2420	1.4290
73.76	1.3189	2.1508	1.3203	1.4732	1.3094	1.0383
88.68	1.4333	1.2830	1.4033	0.9425	1.3244	0.7198
100.00	1.4795	0.8411	1.4458	0.6727	1.4130	0.5328

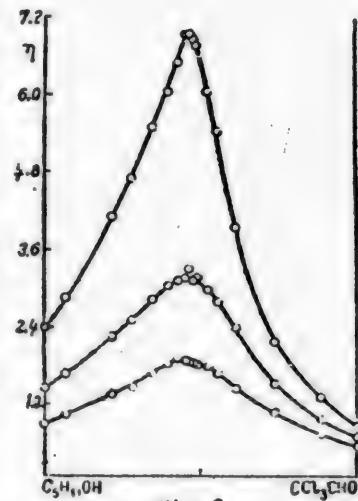


Fig. 2

Methyl alcohol was dried and distilled over quicklime. The distillation of alcohol was carried out by using a 2 m. column, packed with glass spirals, 5 mm in diameter and 1 mm thick. The boiling point of methyl alcohol was 64°C at 732 mm. pressure.

Isoamyl (inactive) alcohol was prepared from the technical product by distillation, using the same column. The fraction used for investigation had an angle of rotation 0.10° . This corresponds to 1.6% of an admixture with the active alcohol. The boiling point of this fraction was 129°C at 721 mm. pressure.

The results on the viscosity and density in the investigation of the system chloral — methyl alcohol are given in Table 1 and graphically presented in Fig. 1. The isotherm viscosities show on the curves a sharply defined maximum, which does not correspond to any regular composition; with a rise in temperature it is shifted slightly towards the alcohol.

The results of the investigation of the chloral — isoamyl alcohol system are given in Table 2 and graphically presented in Fig. 2. The viscosity isotherms pass through a sharply defined maximum, which also, being shifted towards the alcohol, does not correspond to a regular ratio of components.

In an examination of the viscosity diagram of the chloral — methyl alcohol and chloral — isoamyl alcohol systems it can be seen that the maximum on the viscosity isotherms is shifted toward the alcohol whether the viscosity of the alcohol is greater or less than the viscosity of the chloral. And since the resulting chloral-alcoholate compounds are stable, they do not dissociate into the original components. It is therefore impossible to interpret the shifting of the maximum toward the alcohol in terms of a dissociation of the compound. In these systems the viscosity maximum is shifted toward the alcohol as a result of its action with the chloral-alcoholates. But since the maximum on the viscosity isotherms is noticeably simplified with the rise in temperature, it can be concluded that the products of the action of the chloral-alcoholates with the alcohols are unstable and dissociate into their individual components with a rise in temperature.

CONCLUSIONS.

1. An investigation has been made of the chloral — methyl alcohol and chloral — isoamyl alcohol systems based on a determination of the viscosity and the density at three temperatures.
2. It has been shown that the viscosity maximum in the alcohol — chloral systems is always shifted toward the alcohol, independent of the magnitude of the viscosity of the latter.

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PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ NITROBENZENE
ELECTROCONDUCTIVITY, VISCOSITY AND SPECIFIC GRAVITY

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The present investigation represents a continuation of an investigation of the electrical conductivity, viscosity and specific gravity of electrolytic solutions in nitrobenzene.

Our investigations of the solutions. $\text{NaCl} \cdot \text{Al}_2\text{Br}_6$ [1]; $\text{KBr} \cdot \text{Al}_2\text{Br}_6$ [2]; $\text{NaBr} \cdot \text{Al}_2\text{Br}_6$ [3] in nitrobenzene have shown that the molecular electrical conductivity has a normal character.

Introducing a correction for the viscosity, the corrected molecular electrical conductivity of these concentrated solutions has an anomalous character.

A comparison of the course of the molecular electrical conductivity curves, taking into account the viscosity in the region of high concentrations, suggests that the molecular state of the substances also is the same; therefore, the course of the M-S curves for the given electrolytic solutions is the same and differs only by its absolute value. In order to investigate the electrical conductivity as a function of viscosity on other electrolytes, an investigation has been made of the electrical conductivity, viscosity and specific gravity of the $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ - nitrobenzene system in the range of concentrations 5.01 - 60.25% and in the temperature interval 20-50°C.

For investigation, $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ was selected based on the data of thermal analysis [4] which show the melt produces a similar compound.

Starting Materials

Aluminum bromide was prepared by the method of Gustavson [5] from aluminum shavings and bromine. The preparation was purified by repeated distillation and collected into ampules. Nitrobenzene was prepared from thiophene-free benzene. The benzene was nitrated by the usual method [6]. the nitrobenzene was washed with a water - soda solution, and dried over calcium chloride. Nitrobenzene, redistilled several times, was collected in ampules. Aluminum bromine was purified by repeated recrystallization and dried to remove moisture. All preparations were stored in sealed ampules. The concentrations of nitrobenzene solutions were adjusted so as to measure simultaneously the electrical conductivity, viscosity and specific gravity. The solution was first of a straw yellow color and with the increase of concentration turned cherry red. The electrical conductivity was measured by the usual Wheatstone bridge and telephone method. As a source of alternating current a generator was used, fed from a line current. The investigations of electrical conductivity were carried out in an Arrhenius vessel fitted with a ground glass stopper and horizontal platinum electrodes.

Electrical Conductivity

Investigations of the electrical conductivity of the $\text{NH}_4\text{Br} \cdot \text{AlBr}_3$ system in nitrobenzene [1], benzene [6], xylene [7], and ethyl bromide [8] have shown that with an increase in

Table 1
 $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene at a temp. of 20°C.

Weight % of complex	$x \cdot 10^3$	$x_1 \cdot 10^3$	S	M	M_1
5.01	2.335	2.690	10160	23.7236	26.4165
10.17	4.027	5.215	4856	19.5551	25.3257
15.10	5.122	7.8665	3159	16.1803	24.8593
20.28	5.714	10.629	2279	13.0222	24.2251
25.54	5.850	13.745	1746	10.2141	24.3484
30.64	5.637	17.304	1403	7.9787	24.2785
35.42	5.141	20.001	1136	5.7864	24.7640
39.24	4.620	25.297	1014	4.6°46	25.2900
45.61	3.507	30.415	844	2.9599	25.6706
50.33	2.674	36.377	736	1.9380	26.7730
60.25	1.149	56.433	566	0.6503	31.9152

Table 2
 $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene at a temp. of 30°C

Weight % of complex	$x \cdot 10^3$	$x_1 \cdot 10^3$	S	M	M_1
5.01	2.657	3.248	10238	27.2023	30.6653
10.17	4.640	5.787	4884	22.6617	28.2664
15.10	6.023	8.971	3183	19.1712	28.8870
20.28	6.796	11.669	2297	15.6104	26.8056
25.54	7.145	15.148	1760	12.5752	26.6609
30.64	7.053	18.582	1416	9.9870	26.3120
35.42	6.586	22.959	1146	7.856	26.3111
39.24	5.924	25.748	1022	6.0543	26.3140
45.61	4.991	29.199	851	4.2473	28.3598
50.33	4.096	37.639	742	3.0392	28.6080
60.25	2.163	56.204	571	1.2350	32.8415

Table 3
 $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene at a temp. of 40°C. 40°

Weight % of complex	$x \cdot 10^3$	$x_1 \cdot 10^3$	S	M	M_1
15.01	3.029	3.169	10300	31.2289	39.4987
10.17	5.282	4.2037	4622	24.4113	33.5810
15.10	6.800	9.425	3210	21.8280	34.5555
20.28	7.935	12.470	2315	18.3648	30.7597
25.54	8.476	16.006	1773	15.0279	30.0968
30.64	8.429	19.401	1425	12.0113	29.5667
35.42	8.099	23.997	1153	9.3381	27.6420
39.24	7.550	26.341	1029	7.7689	29.50
45.61	6.560	33.091	857	5.6219	28.3593
50.33	5.619	38.246	748	4.2030	28.6080
60.25	3.454	56.365	575	1.9860	32.8415

Table 4
 $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene at a temp. of 50°C.

Weight % of complex	$x \cdot 10^3$	$x_1 \cdot 10^3$	S	M	M_1
5.01	3.375	3.395	10400	35.1060	39.4987
10.17	5.980	6.763	4962	29.6727	33.5610
15.10	7.781	10.069	3235	25.1715	32.5555
20.28	8.974	13.190	2332	20.9273	30.7597
25.54	9.743	16.842	1787	17.4107	30.0968
30.64	9.905	20.574	1437	14.2334	29.5667
35.42	9.675	25.234	1163	11.2520	29.3488
39.24	9.113	28.447	1037	9.4501	29.500
45.61	8.249	34.759	854	7.1241	30.0320
50.33	7.436	40.481	769	5.6885	30.8470
60.25	4.915	57.442	579	2.8457	33.2584

Table 5

Specific gravity d_4^{25} of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

Weight % of complex	20°	30°	40°	50°
5.01	1.2402	1.2307	1.2218	1.2114
10.17	1.2783	1.2708	1.2610	1.2509
15.10	1.3231	1.3128	1.3021	1.2915
20.28	1.3662	1.3555	1.3440	1.3349
25.54	1.4154	1.4013	1.3959	1.3831
30.64	1.4660	1.4516	1.4458	1.4332
35.42	1.5179	1.5061	1.4946	1.4832
39.24	1.5623	1.5516	1.5437	1.5324
45.61	1.6393	1.6265	1.6146	1.6024
50.33	1.7027	1.6891	1.6767	1.6644
60.25	1.8187	1.8357	1.8227	1.8097

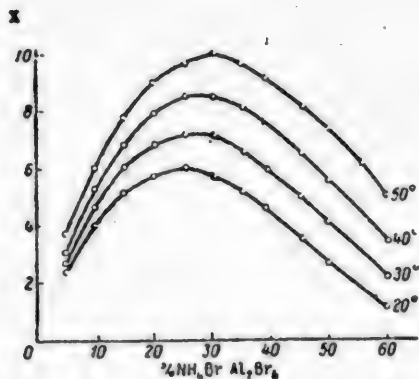
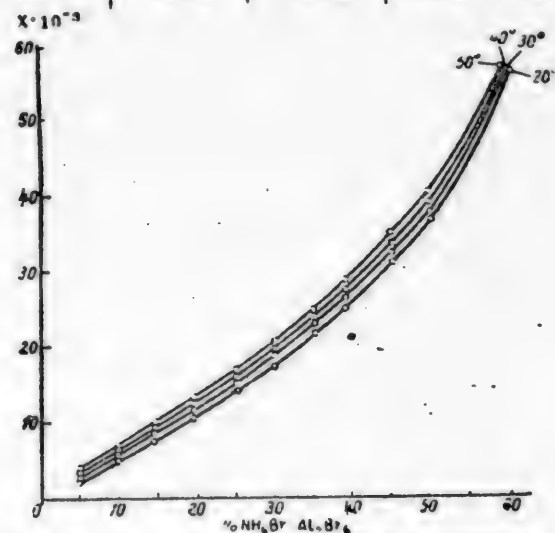
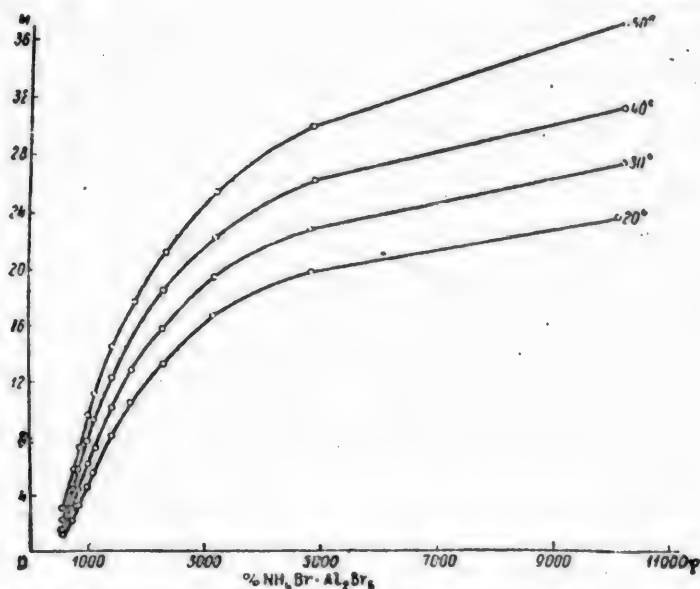
Fig. 1. Specific electrical conductivity of solution of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene.

Table 6

Viscosity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

Weight % of complex	20° n-10°	30° n-10°	40° n-10°	50° n-10°
5.01	2.2493	2.0541	1.9067	1.2576
10.17	2.9160	2.6955	1.6913	1.4138
15.10	3.1024	2.5023	1.9982	1.6176
20.28	3.7578	2.8848	2.2630	1.8373
25.54	4.8153	3.5618	2.7194	2.1606
30.64	6.2011	4.4262	3.3146	2.5965
35.24	8.6450	5.8566	4.2625	3.2804
39.24	11.0610	7.3020	5.4241	3.9021
45.61	17.5191	9.8293	7.2640	5.2673
50.33	27.4805	15.4379	9.8016	6.8050
60.25	99.2124	43.7175	23.4992	14.4691

Fig. 2. Specific electrical conductivity corrected for viscosity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene.Fig. 3. Molecular electrical conductivity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

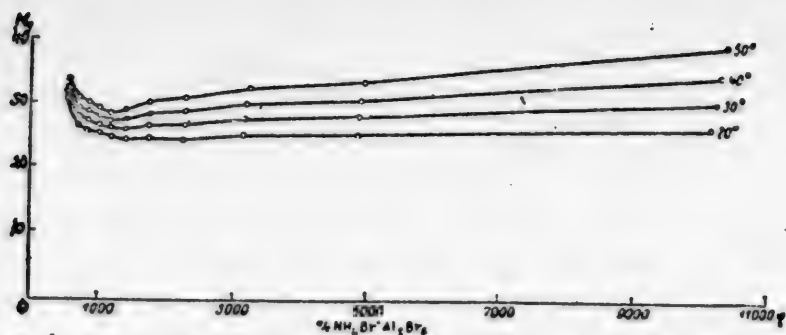


Fig. 4. Corrected molecular electrical conductivity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

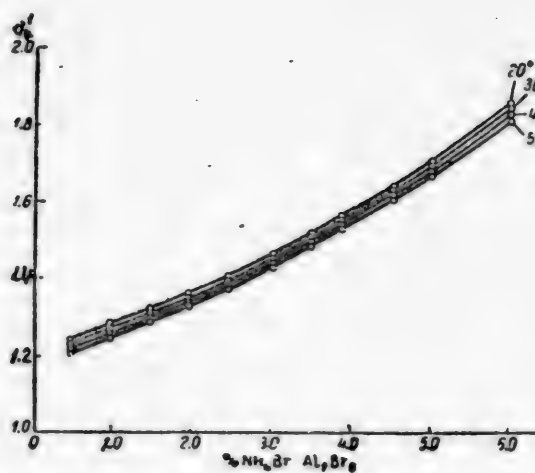


Fig. 5. Specific gravity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

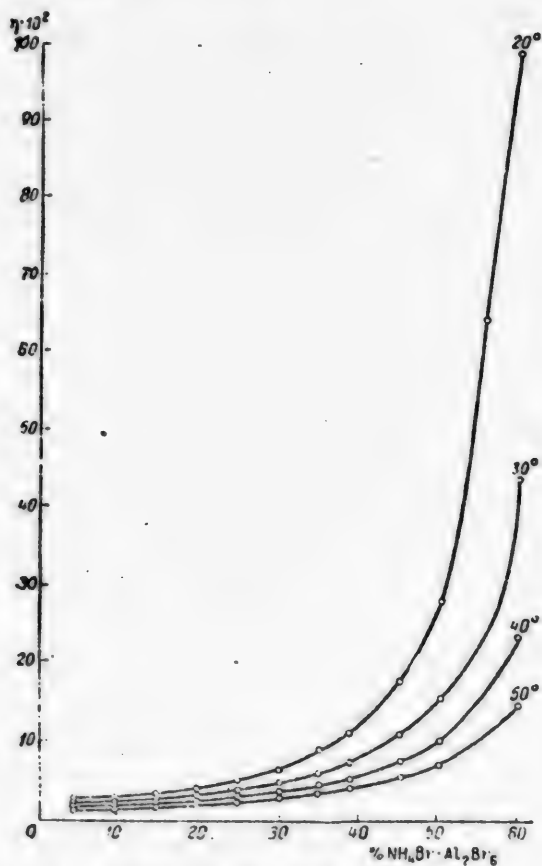


Fig. 6. Viscosity of solutions of $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene

concentration of the ammonium bromide, the specific electrical conductivity increases. A considerable increase in the values of electrical conductivity of these ternary systems as compared with the binary -- aluminum bromide -- an organic solvent occurs. The authors ascribed this increase to the formation of complexes which passed the current.

The results on measuring the specific electrical conductivity of the system $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6 - \text{C}_6\text{H}_5\text{NO}_2$ are given in Tables 1-4 and presented graphically in Fig. 1. On the abscissa are given the weight percentage of the complex, and on the ordinate -- the specific electrical conductivity in reciprocal ohms. The curves in Fig. 1 relate the specific electrical conductivity as a function of temperature and concentration. As shown in Fig. 1, the value of the specific electrical conductivity increases with the increase in concentration, passes through the maximum, and then, with a further increase in concentration, is gradually lowered. The maximum on the curves corresponds to 25-30% of complex. With an increase in temperature, the specific electrical conductivity increases linearly for high concentrations. The rise in temperature shifts the maximum on the curves of high concentration.

The results of calculations of specific electrical conductivity, corrected for viscosity, are given in Tables 1-4 and presented graphically in Fig. 2. As Tables 1-4 and Fig. 2 show, by introducing a correction for viscosity the maximum of the electrical conductivity disappears, and the curves increase and become concave toward the abscissa with an increase in the concentration of the electrolyte. The increase in temperature has a slight influence on the corrected specific electrical conductivity.

The calculation of molecular electrical conductivity was conducted, starting with the complex $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$, at different temperatures and concentrations. The results are given in Tables 1-4 and presented graphically in Fig. 3.

As Tables 1-4 and Fig. 3 show, the value of molecular electrical conductivity increases with dilution and is normal in nature with respect to its aqueous solutions. With a rise in temperature, the value of the molecular electrical conductivity increases linearly. It is of interest to follow the character of the curves of anomalous molecular electrical conductivity of solutions under investigation in the region of high concentrations. For this purpose, a calculation was made of the molecular electrical conductivity corrected for the viscosity of the solution. In Tables 1-4 are summarized the values of molecular electrical conductivity, corrected for viscosity, and these are shown graphically in Fig. 4. The course of the curves (Fig. 4) of electrical conductivity corrected for the viscosity of this system behaves as in previous investigations. With an increase in concentration, the curve first decreases, passes through a minimum, and then gradually increases. With an increase in the concentration of the complex, the number of the structural groups and the extent of the regularity of the electrolyte increase [1]

As a result, the molecular electrical conductivity corrected for viscosity in the region of concentrated solutions has an anomalous character. With a rise in temperature, the value of the corrected molecular electrical conductivity, as a result of the decrease in the viscosity of the solution, results in an increase of these values.

By analogy in the course of corrected molecular electrical conductivity for the complexes under investigation $\text{NaCl} \cdot \text{Al}_2\text{Br}_6$, $\text{KBr} \cdot \text{Al}_2\text{Br}_6$, $\text{NaBr} \cdot \text{Al}_2\text{Br}_6$, $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene one may assume that both the molecular state of these substances in solution and the structural groups (associates) which are formed are similar. Hence, it follows that the mechanism of the passage of the electric current in the electrolytic solutions under investigation are also similar. It is believed that in the solution under investigation the course of anomalous molecular electrical conductivity is to a considerable extent affected by the factors: viscosity of solutions, number of structural groups inhibiting the action of the ionic bond, and other factors taking place in solution.

Specific Gravity

The investigation of the specific gravity of the complex in nitrobenzene was conducted under the same conditions as the electrical conductivity. The specific gravity was measured in a pycnometer fitted with a ground stopper with 0.01 ml. divisions.

The results of the determination of specific gravity are summarized in Table 5 and presented graphically in Fig. 5.

As Table 5 indicates, the values of the specific gravity increase with an increase in concentration, and the curves in Fig. 5 are concave toward the abscissa. The rise in temperature results in a decrease of the specific gravity which varies linearly.

Viscosity

The viscosity of the solution under investigation was determined under the same conditions as the electrical conductivity and the specific gravity.

The measurement of viscosity of the solution under investigation was determined in a modified Ostwald's viscometer [12]. The viscosity was calculated from the formula

$$\eta_0 = \frac{d_p \cdot t_p}{d_0 \cdot t_0} \cdot \eta_{\text{abs.}}$$

where d_p and t_p are the specific gravity and time of flow of solution; d_0 and t_0 specific gravity and time of flow of water at the same temperature; $\eta_{\text{abs.}}$ of water taken from tables [13]. The results are summarized in Table 6 and presented graphically in Fig. 6.

The curves in Fig. 6 represent the viscosity as a function of temperature and concentration of solution.

As Table 6 and Fig. 6 indicate, the values of the viscosity of solutions at low concentrations of complex first slightly increase and the curve slopes downward; further, with an increase in concentration of the complex, the curvature of the curve is sharply increased.

Conclusions

1. The electrical conductivity, viscosity and specific gravity of the complex $\text{NH}_4\text{O}_2 \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene in the range of concentration from 5.01 to 60.25%, in the range of temperatures 20, 30, 40 and 50°C have been investigated.
2. Correcting for viscosity, the maximum on the curves of specific electrical conductivity disappears, and the molecular electrical conductivity exhibits an anomalous character.
3. An analogy in the shape of the curves for electrical conductivity, viscosity and specific gravity of the investigated complexes $\text{NaCl} \cdot \text{Cl}_2\text{Br}_6$, $\text{KBr} \cdot \text{Al}_2\text{Br}_6$, $\text{NaBr} \cdot \text{Al}_2\text{Br}_6$ and $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene indicates that the nature of these systems is, apparently, similar.
4. The specific and molecular electrical conductivity are increased with a rise in temperature and the viscosity decreased.
5. The specific gravity curves are concave toward the abscissa.

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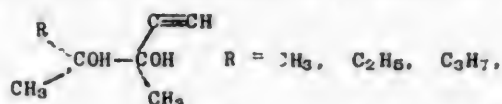
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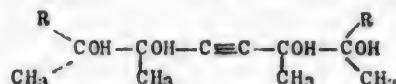
SYNTHESIS OF DIMETHYLETHYNYLPHENYLETHYLENE GLYCOL AND ITS REACTION WITH SULFURIC ACID

T. A. Favorskaya and A. N. Shirshova

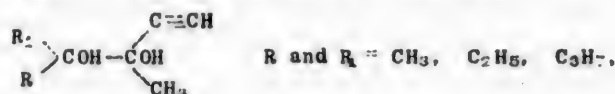
Only a few pinacols containing an unsubstituted acetylene radical are known. A.G. Favorskaya and A.S. Onishchenko [1] obtained a few pinacols of the type:



when heated in vacuo the corresponding erythrites were obtained:

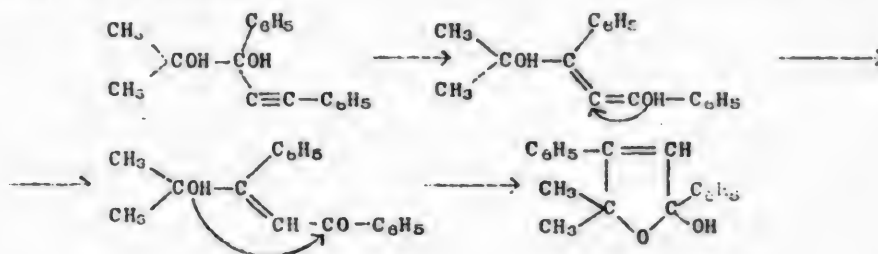


Berthel and Colonge [2] obtained pinacols of the type:



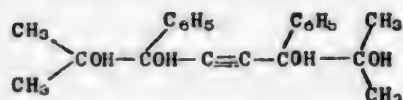
by the condensation of the corresponding keto-alcohols with acetylene in the presence of sodium amide. No study has been made of the isomeric transformations of these glycols.

A. E. Favorskii and E. D. Venus [3]. E. D. Venus - Danilova and E. P. Briciko [4, 5] synthesized a series of pinacols with substituted acetylene radicals: dimethyl-phenyl-phenylethynyl ethylene glycol, dimethyl-phenyl-tertiary butylethynyl-ethylene glycol and dimethyl-p-tolyl phenylethynyl ethylene glycol, and investigated their extremely interesting transformation under the influence of sulfuric acid to the corresponding oxydihydrofuranes, according to the scheme:

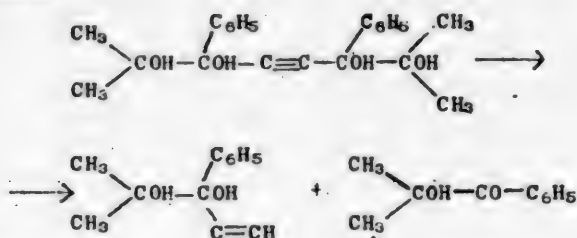


As early as 1913, A.E. Favorsky suggested a synthesis of a pinacol containing a free acetylenic hydrogen ... dimethylethynyl-phenyl ethyleneglycol, and a study of its reaction with sulfuric acid. The work was not completed and the products were stored in sealed containers.

Recently the synthesis of pinacol was repeated by A.N. Shirshova. Pinacol was obtained by the action of dimagnesium dibromoacetylene on dimethylbenzoylcarbinol. It was expected that the reaction product would be the corresponding erythrite:

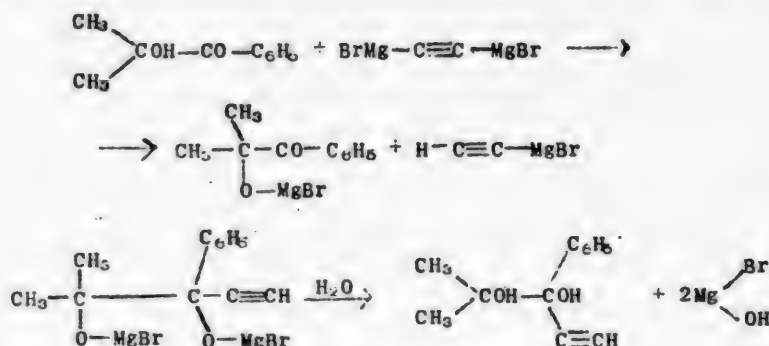


which upon fractional distillation in vacuo would decompose into pinacol and the initial keto-alcohol:



analogous to that observed by A.S. Onischenko in a synthesis of acetylenic erythrites.

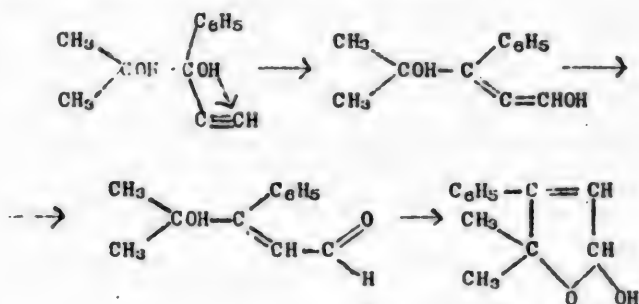
However, the fractional distillation of the reaction products in vacuo yielded only an insignificant amount of the fraction of a b.p. of the initial keto-alcohol, whereas the pinacol was the main reaction product. This disproportion in the amounts of pinacol and keto-alcohol obtained requires the adoption of another mechanism to explain the pinacol formation. Dimagnesium-dibromoacetylene, reacting with the hydroxy group of dimethylbenzoylcarbinol, is transformed to magnesium-bromoacetylene, which reacts with the carbonyl group of the keto-alcohol. Decomposition of the magnesium-organic complex with water yields pinacol:



Among the reaction products in addition to pinacol and a small amount of keto alcohol, identified by a semicarbazone of m.p. 176-177°C. was isolated a fraction of b.p. 94°C at 7 mm. which was identified as dimethylbenzylcarbinol. Its formation can be explained by the fact that under the conditions of magnesium organic synthesis dimethylbenzyl carbinol was reduced, its carbonyl group being reduced to a CH₂ group. To formulate a reaction mechanism at this stage would be premature. The reducing properties of magnesium organic compounds have been known for a long time and have been studied on a series of examples; however, the reducing properties of magnesium-bromoacetylene have not been described in the literature: in addition, the reduction of the carbonyl group under the influence of magnesium-organic compounds always yields a secondary alcohol group; in this case there was a complete reduction to the CH₂ group.

The main reaction product was pinacol -- dimethyl-ethynyl-phenyl-ethylene glycol of a m.p. of 28°C; it contains free acetylenic hydrogen, and forms a white flaky precipitate with an ammoniacal solution of silver oxide. When heated with a sodium hydroxide solution it decomposes to acetylene and keto alcohol - dimethylbenzoylcarbinol. Oxidation of the pinacol with lead tetraacetate by the method of Grieg [6] yields acetone; the second decomposition product, benzoylacetylene, formed a resinous substance under these reaction conditions.

A study was made of the interaction of the pinacol with dilute sulfuric acid. Heating with 20 and 10% sulfuric acid gave rise in both cases to resins. Boiling for a longer period (for two hours), after the removal of resin the acidic aqueous solution had a yellow-green fluorescence, which disappeared upon neutralization of the solution. No other products than the starting material, pinacol, could be isolated either from the acidic or neutral solutions. The results suggest that in the interaction of dimethyl-ethynyl-phenyl-ethylene glycol, the transformation proceeds according to the scheme established by E.D. Venus-Danilova for pinacols with substituted acetylenic radicals. The derivatives of hydroxydihydrofurane formed, when dissolved in mineral acids have a green fluorescence and form oxonium salts. The derivatives of hydroxydihydrofurane react in the tautomeric form of unsaturated ketoalcohol; in the case of dimethyl-phenyl-tertiary butyl ethynyl ethylene glycol the unsaturated hydroxyketone was isolated in a free state. In our case an unsaturated hydroxyaldehyde instead of hydroxyketone should be formed; in the presence of sulfuric acid this is almost completely resinified, and only a small part yields a derivative of hydroxydihydrofurane; its presence in an acid solution can be detected from a weak, but fairly clear, yellow-green fluorescence:

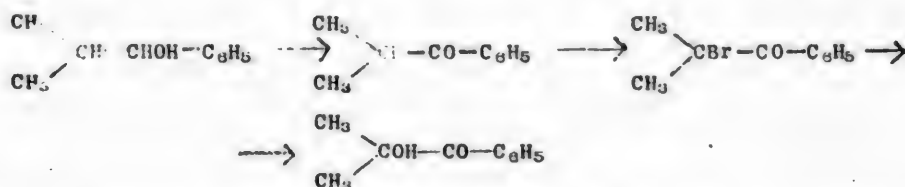


The absence of carbonyl derivatives in the reaction products indicates that a second possible isomeric conversion of pinacol - pinacolone rearrangement takes no place in this case.

EXPERIMENTAL

1. Synthesis of dimethyl ethynyl phenyl-ethylene glycol

The initial dimethylbenzoylcarbinol was obtained by the ordinary method of gradual transformations:



The saponification of bromoketone was carried out by using an aqueous-alcoholic solution of sodium hydroxide by the method of Auwers and Mauss [7]. The saponification was completed

in 4½ hours, yield of ketoalcohol 80%.

Into an ethereal solution of magnesium-bromoethyl (obtained from 25 g. magnesium and 113 g. ethyl bromide in 400 ml. ether), was passed a current of acetylene at 0°C, until the reaction mixture showed a definite separation into layers. On the following day 85 g. of ketoalcohol in 400 ml. alcohol was added slowly with efficient stirring, over a period of 9 hours, to the magnesium-organic compound. Upon completion of addition of the ketoalcohol, the stirring was continued for another 2 hours, and the product allowed to stand overnight. After decomposition of the magnesium-organic complex with water and dilute sulfuric acid, the ether layer was separated, and the extract dried with potassium carbonate. After distilling off ether the residue was subjected to repeated fractional distillation in vacuo. Three fractions were collected under a pressure of 7 mm.

I 94-95°C -- 24%; II 110-115°C -- 4%; III 140-143°C -- 45%.

The first two fractions are liquid, the third fraction crystallized in the receiver. Boiling points of I and III fractions are similar to those of the products synthesized in 1913; the products remained entirely unchanged, boiled and melted as 25 years ago, and could be used for subsequent investigations.

The boiling point of fraction II indicated the possible presence of the initial ketoalcohol (b.p. 115-116°C at 7 mm). Treatment with semicarbazide hydrochloride yielded a small amount of semicarbazone of m.p. 176-177°C; the greater part of the substance taken for the reaction remained unchanged as a liquid, insoluble in the semicarbazide solution. When mixed with the known semicarbazone gave no depression of the melting point.

Analysis of semicarbazone of m.p. 176-177°C

0.0852 g. substance:	13.9 ml N ₂ (20°, 762 mm).
0.0940 g. substance:	15.5 ml N ₂ (19°, 760 mm).
Found %:	N 18.8, 19.03
C ₁₁ H ₁₅ O ₂ N ₃ . Calculated %:	N 19.00.

2. Investigation of fraction of b.p. 94-95°C at 7 mm.

B.p. of fraction (11 mm) -- 103-104°C. A careful fractionation yielded a fraction of b.p. 94°C at 7 mm. This fraction forms no semicarbazone.

Analysis of substances of b.p. 94°C at 7 mm.

Determination of elemental composition

0.1189 g. substance	0.3480 g. CO ₂ :	0.1004 g. H ₂ O.
0.1228 g. substance	0.3593 g. CO ₂ :	0.1029 g. H ₂ O.
Found %:	C 79.82, 79.93:	H 9.45, 9.39
C ₁₁ H ₁₄ O. Calculated %:	C 80.00;	H 9.33.

Determination of hydroxyl, by the method of Chugarev-Zerevitinov

0.0705 g. substance:	10.2 ml. CH ₄ (16.5°C, 740 mm)
Found %:	OH 10.07.
C ₁₁ H ₁₄ O(OH). Calculated %:	OH 11.33.

In the determination of the hydroxyl group, the magnesium organic compound rapidly absorbed oxygen from the air: this was responsible for the low results obtained.

Determination of molecular weight

0.1373 g. substance:	18.66 g. benzene: Δt 0.25°
0.1533 g. substance:	20.71 g. benzene: Δt 0.25°
Found:	M 150.9, 152.0.
C ₁₁ H ₁₄ O. Calculated:	M 150.0.

Determination of specific gravity and molecular refraction

d ₄ ²⁰ 1.0090:	d ₄ ²⁵ 0.9934;	d ₄ ²⁰ 0.9929;	n _D ²⁰ 1.5188.
Found: MR _D	45.81.		
C ₁₁ H ₁₄ O(OH) F. Calculated:	MR _D	45.97.	

The absence of a carbonyl group in the substance boiling at 94°C at 7 mm. and the similarity in the constants given in the literature for methylbenzylcarbinol:

B.p. 103-105°C at 10 mm; d_4^{20} 0.9774; M_R 45.99,

indicate that the fraction of b.p. 94°C at 7 mm (103-104°C at 11 mm) is dimethylbenzylcarbinol.

This alcohol gives no discoloration of the permanganate solution in the cold; on oxidation with chromic mixture, it is recovered unchanged. When boiled with 1% potassium permanganate solution the alcohol was recovered in part, and part was oxidized to CO₂ and benzoic acid. This behaviour towards oxidation indicates the presence of a tertiary alcoholic group in the alcohol.

3. Investigation of the fraction of b.p. 133-144°C at 7 mm.

This fraction, representing dimethyl-ethynyl-phenyl-ethyleneglycol, crystallizes in the receiver and partly in the condenser, with the formation of pretty druses of crystals. The melting point of the product recrystallized from a mixture of ether and petroleum ether was 77-78°C. Treatment of the pinacol with an ammoniacal solution of silver oxide yielded a white, flaky precipitate of the silver derivative. Pinacol is sparingly soluble in benzene.

Analysis of the substance of m.p. 77-78°C

Determination of elemental composition

0.0970 g. substance: 0.2689 g. CO₂; 0.0649 g. H₂O.
0.2066 g. substance: 0.5729 g. CO₂; 0.1373 g. H₂O.
Found %: C 75.60, 75.63; H 7.50, 7.44.
Calculated %: C 75.79; H 7.37.

Determination of molecular weight

0.1043 g. substance; 28.92 g. benzene: Δt 0.10°.
Found: M 185.
C₁₂H₈O₂. Calculated: M 190.

4. Decomposition of pinacol by heating with alkali.

8 g. pinacol was heated with 10 g. of sodium hydroxide, and dissolved in 40 ml. water; the liberated acetylene was absorbed by the copper reagent, prepared according to Ilosway, a characteristic red-meat precipitate of the copper derivative being formed. The reaction mixture (strongly tarred) was subjected to steam distillation. The distillate was extracted with ether; distilling of the ether yielded a small amount of ketoalcohol of b.p. 112-117°C at 7 mm.

5. Oxidation of pinacol by means of lead tetraacetate.

Lead tetraacetate was prepared by the method of Criege from red lead and glacial acetic acid. 3.5 g. of pinacol dissolved in 30 ml. of glacial acetic acid, and 10 g. (2 g. in excess) of lead tetraacetate were placed in a vessel fitted with a reflux condenser. Upon mixing the reaction products, heat was evolved. When heated in a water bath at a temperature of 50-60°C. lead tetraacetate dissolved completely in one hour. After cooling, the contents were neutralized with soda, the precipitate of mineral salts filtered off, and the filtrate distilled off. The first drops of distillate were treated with a solution of p-nitrophenylhydrazine. The precipitated p-nitrophenylhydrazone of m.p. 146°C gave no depression with p-nitrophenylhydrazone of the known ketone. The subsequent drops yielded a small white flaky precipitate with an ammoniacal solution of silver oxide; this indicates the presence in the aqueous solution of benzoylacetylene, the second decomposition product of glycol; the main mass of this unsaturated ketone remained in the distilling flask as a resin.

6. Reaction of glycol with sulfuric acid.

10 g. of pinacol was heated to boiling with constant stirring with 115 ml. 20% sulfuric acid for 15 minutes. The liquid darkened strongly and the heating was discontinued. The

reaction products, with the exception of a small amount of recovered initial glycol (b.p. 145-148°C at 13 mm, m.p. 70-77°C) could be recovered either from the acidic solution, or the solution neutralized with soda.

In order to reduce tarring, the following experiment was carried out using 10% sulfuric acid. 10 g. pinacol was heated with 128 ml. 10% sulfuric acid. Disregarding the pronounced darkening of the solution, the boiling was continued for 2 hours. Upon completion of boiling, the solution was decanted from a large amount of a sticky, thick dark resin. Upon cooling, the solution yielded a small amount of pinacol of m.p. 76°C. The crystals were filtered out; the solution had a weak, but a definite yellow-green fluorescence. Upon neutralization with soda the fluorescence disappeared. No products were isolated from the solution.

CONCLUSIONS

1. Dimethyl-ethynyl-phenyl-ethyleneglycol has been synthesized.
2. It has been shown that in its preparation, the ketoalcohol of dimethylbenzoylcarbinol is reduced to dimethylbenzyl carbinol.
3. The structure of the glycol was verified by decomposing it by heating it with a solution of alkali, and by oxidizing it with lead tetraacetate.
4. The reaction of the glycol with 10 and 20% sulfuric acid has been investigated.

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OXIDATIVE AND OXIDATIVE - HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

IV. OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF 2-METHYL-1,4-NAPHTHOQUINONE OXIDE

L. A. Shchukina, A. P. Kondrat'eva, and M. M. Shemyakin

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the USSR

In an earlier communication [1] it was emphasized that in order to understand the causes and mechanism of purely hydrolytic, as well as oxidative-hydrolytic cleavages of quinones it was essential to know whether a preliminary treatment of quinones with oxidizing agents promotes their hydrolytic cleavage.

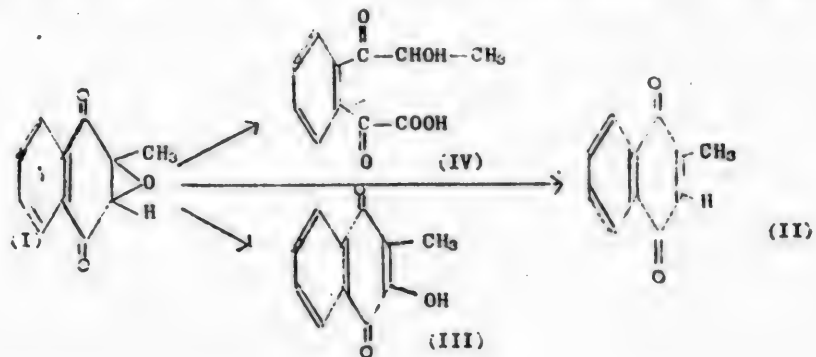
Since this problem was unsolved, it seemed desirable to make a systematic investigation, starting at first with quinone oxides. These should be primary compounds, which may be formed by the action of oxidizing agents on quinones; therefore, it was of interest to clarify not only the principal tendency of the ring groupings toward hydrolytic cleavage, but also the conditions under which this process could be realized.

Clarification of these problems should answer this question: does the entering of the oxide oxygen into the molecule facilitate or hinder the hydrolytic cleavage of carbon bonds?

In an attempt to obtain comparable results, the 2-methyl-1,4-naphthoquinone oxide (I) was selected for the initial investigation, since earlier studies had covered the character and conditions of cleavage of the cyclic groupings 2-methyl-1,4 naphthoquinone (II) [2] and 2-methyl-3-hydroxy-1,4 naphthoquinone (phthiocol), (III) [3].

According to our data, described in detail in the experimental section and in a subsequent communication [4], the process of the cleavage of 2-methyl-1,4-naphthoquinone oxide differs with respect to the conditions necessary and the inherent nature of the reaction occurring in the cleavage of 2-methyl-1,4-naphthoquinone and phthiocol. Whereas the two last-named compounds remain practically unchanged by prolonged heating with water in the presence or absence of oxygen, if the initial pH value of the solution is 7, 2-methyl-1,4-naphthoquinone oxide may exhibit under these conditions cleavage of the carbon bonds in the ring.

The formation of o-lactyl-phenyl-glyoxylic acid (IV) is a result of such a process. The initial oxide is partially converted to 2-methyl-1,4-naphthoquinone (II), and phthiocol (III).



The formation of o-lactyl phenyl-glyoxylic acid (IV) is not only due to the hydrolyzing action of the sodium. As will be shown in a subsequent communication, 2-methyl-1,4-naphthoquinone oxide undergoes under these conditions a series of oxidative-hydrolytic transformations; in addition to oxygen from the air, the initial oxide and the reaction product 2-methyl-1,4-naphthoquinone may act as oxidizing agents.

Thus, the cleavage of the oxide (I) to the acid (IV) should be regarded as an oxidation-reduction process. In this respect this differs greatly from the purely hydrolytic cleavage of phthiocol [3] not connected with a concurrent action of any oxidizing agent.

The separation of the reaction products, formed after boiling 2-methyl-1,4-naphthoquinone with water presents no difficulties. The presence of 2-methyl-1,4-naphthoquinone and phthiocol among the reaction products (see experimental section) can be determined without difficulty. However, to establish the structure of o-lactyl phenyl-glyoxylic acid (IV), not described in the literature, required special investigation.

This acid appeared as a white crystalline substance, melting, with decomposition, at 232°C. The results of titration and of the analytical data on the silver salt indicated that it is a monocarboxylic acid. Boiling with methyl or ethyl alcohol in the presence of sulfuric acid yielded the corresponding monoesters. The methyl ester of this acid was also obtained by the action of methyl iodide on the silver salt. According to the data on elemental analysis of these esters and the acid, the formula of the acid corresponds to $C_{11}H_{10}O_6$. The acid (IV) developed a bright yellow coloration with a solution of ferric chloride. This suggests the presence of an enol hydroxyl. However, the preparation of a derivative with respect to the hydroxyl group is difficult. Acetylation with acetic anhydride or acetyl chloride in the presence or absence of pyridine yielded no individual compounds. The acid (IV) did not discolor bromine water, but underwent oxidation in an aqueous solution. With an ammoniacal silver solution, it formed a silver mirror; but it gave no corresponding derivatives with sodium bisulfite and no corresponding derivatives with p-nitrophenylhydrazine and semicarbazine. The acid (IV) was fairly resistant to hydrolytic cleavage. It was practically unchanged on prolonged boiling with 1% aqueous sulfuric acid, and also in an aqueous buffer solution at pH 7.2. However, at a higher pH value, it may undergo changes (see below). Thus, the preliminary investigation has established definitely only the presence of one carboxyl group in the molecule. The presence of carbonyl and hydroxyl groups could not be confirmed, although the 5 oxygen atoms and a positive reaction with ammoniacal silver suggested their presence.

Liben's reaction was found to be essential to clarify the structure of the acid (IV). Heating the alkaline solution of this acid with iodine yielded iodoform.

This suggests that the molecule contains either the group $COCH_3$, or the group $CH(OH)-CH_3$. Therefore, the acid (IV) is not a bicyclic compound.

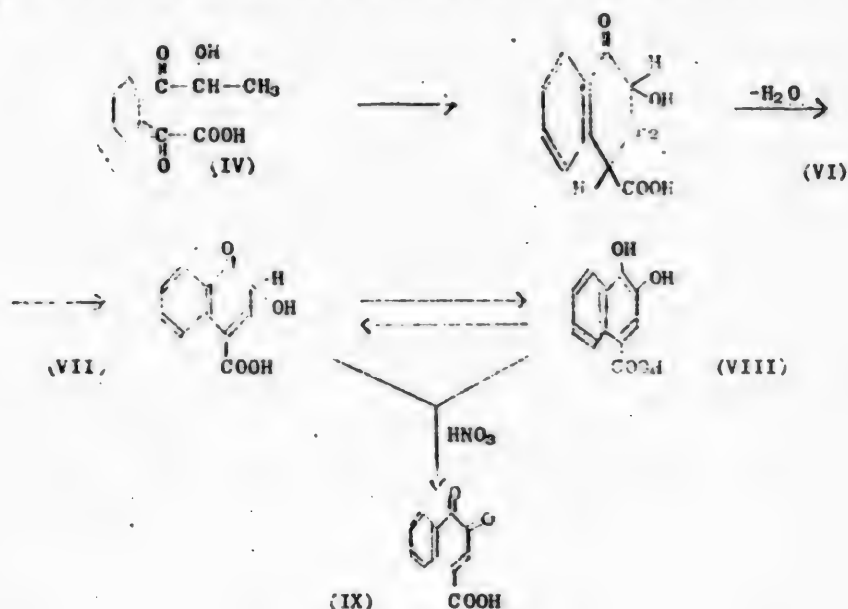
The observation of the behavior of the acid (IV) in alkaline solution was found to be of still greater importance. It was established that aqueous acid developed a red coloration in the presence of alkali, when shaken in air -- slowly in the cold, and rapidly when heated. It was found that the development of the red color was connected with the formation of a red alkaline salt of 2-hydroxy-1,4-naphthoquinone (V). The latter separated as a yellow precipitate when the solution was acidified. It can be identified by its melting point, and also by a synthesis of various derivatives described in the literature. Under certain conditions (see experimental section) 2-hydroxy-1,4-naphthoquinone can be obtained from acid (IV) with a yield approaching 90% of theoretical.

Since this reaction was of great importance for a final confirmation of the acid structure (IV), it was investigated in detail. These transformations are also of interest since they provide better understanding of the mechanism of the ring closure of such compounds with respect to quinones. In particular, the investigation of this reaction made possible a study of the mechanism of the so called Kooker reaction involving the opening of the quinone ring and its subsequent formation. [1].

With respect to confirmation of the acid structure (IV), we find that the formation of 2-hydroxy-1,4-naphthoquinone (V), in which two carbonyl groups are directly combined with the benzene ring suggests that these carbonyl groups should be next to the benzene ring also in the acid (IV). The position of the carboxyl group in the molecule had not been completely verified. It remained uncertain as to whether the molecule contains three ketone groups or one hydroxyl and two ketone groups. To clarify these questions and finally to establish the acid structure (IV), the acid was heated with aqueous alkali in the presence of oxygen from the air. It was found that under these conditions there was no formation of 2-hydroxy-1,4-naphthoquinone. Instead, a crystalline substance of decomposition temperature 194°C having the formula $C_{11}H_6O_4$ was isolated.

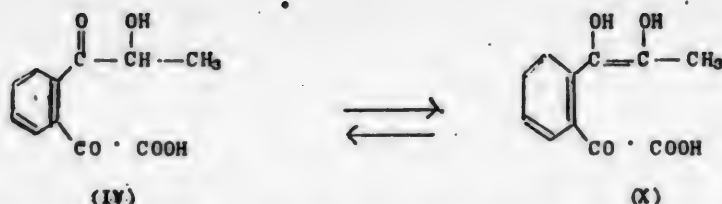
The presence of three active hydrogen atoms was determined by the method of Zerevitinov-Terent'ev. Titration was conducted in hydrogen atmosphere. In an alkaline solution in the presence of oxygen from the air, this compound formed a red alkaline solution of 2-hydroxy-1,4-naphthoquinone. This interfered with an accurate determination of the end point. It was found that this compound was a monocarboxylic acid.

1,2-Naphthohydroquinone-4-carboxylic acid (VIII) was described in the literature and its properties are similar to those of our compound [5]. This acid was prepared by reducing 1,2-naphthoquinone-4-carboxylic acid, of m.p. 164-165°C, and it yielded an anilide of m.p. 260°C [5]. To verify the identity of the product formed in the reaction with 1,2-naphthohydroquinone-4-carboxylic acid it was oxidized with nitric acid. A quinone of orange color with a m.p. 164-165°C was obtained; this formed an anilide of m.p. 260°C. According to the analytical data, the formula of the quinone is $C_{11}H_6O_4$. Thus, no doubt remains that the quinone is 1,2-naphthoquinone-4-carboxylic acid (IX), and the compound of m.p. 194°C is 1,2-naphthohydroquinone-4-carboxylic acid (VIII). The formation of the latter from the acid (IV) when heated with an alkaline solution in the absence of oxygen from the air can be represented in the following scheme.



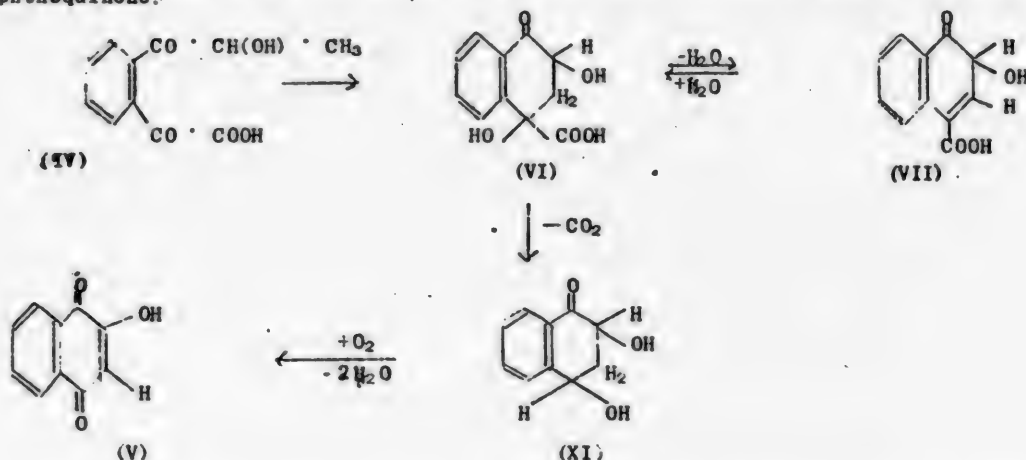
These transformations confirm definitely that the acid (IV) is *o*-lactyl-phenylglyoxylic acid.

It should be pointed out that the latter may react also in the tautomeric form (X):



with the possibility of the formation of a diol grouping; apparently this hinders the preparation of the corresponding derivatives with respect to the hydroxyl and the carbonyl groups.

A further study of the properties of the acid (IV \rightleftharpoons X), and also of the acid (VII \rightleftharpoons VIII) was of interest from the point of view of clarifying the mechanism of formation of 2-hydroxy-1,4-naphthoquinone (V). It has been established that this quinone is obtained by heating with aqueous alkali either the acid (IV \rightleftharpoons X) or the acid (VII \rightleftharpoons VIII). However, in both cases the presence of oxygen from the air was necessary; otherwise the acid (IV \rightleftharpoons X) was transformed to the acid (VII \rightleftharpoons VIII) only. The latter remained unchanged under these conditions. On the other hand it has been shown that the formation of 2-hydroxy-1,4-naphthoquinone is accompanied by a quantitative splitting off of one molecule of carbon dioxide. All these facts suggest the following scheme of transformation of o-lactyl-phenyl-glyoxylic acid to 2-hydroxy-1,4-naphthoquinone:



The first stage in this reaction is, apparently, the formation of an intermediate α -hydroxy acid (VI). A six-membered ring is formed. Similar transformations have been described in the literature; however, they referred only to five-membered transformations (Reference [2] in Communication I). This reaction indicates that such cyclizations lead also to six-membered rings.

The acid (VI) can be isolated as its dehydration product - acid (VII) when the reaction is carried out in the absence of oxygen; this excludes the possibility of oxidative decarboxylation of acid (VI) to 2-hydroxy-1,4-naphthoquinone. Since the acid (VII) can be transformed to 2-hydroxy-1,4-naphthoquinone only in an alkaline solution in the presence of oxygen from the air, it can be assumed that it is first hydrated and then transformed back to the acid (VI); the latter is then subjected to oxidative decarboxylation.

It is of interest to point out the character of this decarboxylation. It has been established that some α -hydroxy acids of structure similar to the indan series can undergo purely hydrolytic decarboxylation without any oxidizing agent being present (data by E. I. Vinogradova, Ya. B. Shvezov, and D. P. Vitrovskii). However, in our case α -hydroxy acid (VI)

was capable of decarboxylation only in the presence of an oxidizing agent: 2-hydroxy-1,4-naphtho-quinone was obtained as a final product. Of course, the formation of the latter should be preceded by more hydrogenated compounds and, probably in the first place by compound (XI).

In conclusion it should be pointed out that the question of the mechanism of transformation of 2-methyl-1,4-naphthoquinone (I), oxide to o-lactyl-phenyl glyoxylic acid (IV) is discussed in detail in a subsequent communication [4]

EXPERIMENTAL*

1. Oxidative-hydrolytic cleavage of 2-methyl-1,4-naphthoquinone oxide

a) In an atmosphere of air. Into a round bottom flask, fitted with a reflux condenser and tube extended to the bottom of the flask and connected with a gasometer, were introduced 2 liters of distilled water. The water was heated to boiling and 3 g. 2-methyl-1,4 naphthoquinone oxide added, and the air allowed to pass from the gasometer. This was continued for 24 hours, and 40-50 l. air was used during this period. The oxide melted in water. After 3-5 minutes the solution developed a pink color which after 15-20 minutes turned to dark yellow. Upon completion of the reaction the solution was cooled, acidified with sulfuric acid and extracted with ether 1-2 times together with the resulting precipitate. The aqueous solution, almost colorless, was evaporated in vacuo at 45-50°C and 5 mm. to a volume of about 150 ml., neutralized with soda to a slightly acid reaction with congo red and then evaporated to dryness. The dry residue was extracted with ether in a Soxhlet apparatus for 15-20 hours. After distilling off the ether a white precipitate remained, slightly contaminated with oily reaction products. The latter were removed and the crystals washed with a small amount of ether. The product was recrystallized 1-2 times from a few ml. of water by using bone black. Yield -- 1.0 g. of o-lactyl-phenyl glyoxylic acid of m.p. 232°C. Yield 28%.

The ether solution was washed several times with a 10% soda solution until the extract became colorless, and then with water to a neutral reaction of the water layer. The neutral ether extract was dried with sodium sulfate and the ether was distilled off. Residue -- 0.15 g. yellow crystalline substance of m.p. 102-104°C. After recrystallization from alcohol m.p. 106°C. In a mixture with 2-methyl-1,4-naphthoquinone the m.p. showed no depression.

The soda solution was acidified with sulfuric acid, the precipitate was filtered off, and the mother-liquor was extracted with ether. After distilling off the ether the compound previously reported was added to the precipitate. Total weight 1.4 g. After recrystallization from methyl alcohol wt. 1.1 g., m.p. 171-172°C. A sample mixed with phthiocol melted at the same temperature.

b) In an atmosphere of hydrogen. A round bottom 3-liter flask was provided with a reflux condenser and an inlet tube extended to the bottom for the passage of hydrogen. The flask was fitted with a cork holding a glass rod with a hook on its end. A glass vessel containing 3 g. of 2-methyl-1,4 naphthoquinone oxide was suspended on the hook. Two liters of distilled water were introduced in the flask. The system was freed from air and filled with hydrogen. This had been purified previously by passing it through an alkaline permanganate solution, pyrogallol and, finally, aqueous lead acetate. In order to remove the last traces of oxygen, hydrogen was passed through an ignited tube filled with copper; after passing through a safety bottle, it was introduced into the reaction flask. The reflux condenser was employed as an outlet for the gas. The condenser was connected to a safety flask and to two Tishchenko flasks containing an alkaline solution of pyrogallol. The displacement of the air

* Acknowledgement is made for the assistance of E.A. Ignat'eva in obtaining the analytical data.

** 2-methyl-1,4-naphthoquinone oxide was obtained by the action of hydrogen peroxide and aqueous soda on the alcoholic solution of 2-methyl-1,4-naphthoquinone. M.p. 102°C from methyl alcohol [6].

from the system was continued for 3 hours. Extra water in the reaction flask being boiled to remove traces of dissolved air. The vessel with the oxide sample was immersed in boiling water and boiling continued for 24 hours while continuously passing through the current of hydrogen. The reaction mixture was also carried out in the presence of hydrogen. The separation of the reaction products and purification were carried out under the conditions described in experiment 1a. Yields: 0.25 g. 2-methyl-1,4-naphthoquinone, 2.3 g. phthalic acid and 0.4 g. o-lactyl-phenyl-glyoxylic acid. Its composition has been investigated.

a) The compound was readily soluble in alcohol, glacial acetic acid, sparingly soluble in ether, very soluble in hot water, less soluble in cold. Yields good crystals from a small amount of water. After three crystallizations from water, m.p. 232°C (with decomposition).

b) In the cold it developed a slight yellow coloration with 10% aqueous alkali. Boiling the alkaline solution in the presence of oxygen from the air developed a garnet red coloration.

c) An aqueous solution of ferric chloride developed a yellow coloration.

d) Bromine water showed no discoloration; an ammoniacal solution of silver nitrate formed a silver mirror only on heating.

e) Yielded no precipitate with lead carbonate either in aqueous or in alcohol solution; this distinguishes this compound from phthalic acid and allows a quantitative determination of the latter when it is present together with the above compound by use of the method described in communication II [2].

f) The substance remained unchanged when boiled for 24 hours with 1% aqueous sulfuric acid, and also when boiled in a buffer solution at pH = 7.21.

g) Analytical data (the substance dried to constant weight at 100-105°C at 5 mm):

Found %: C 59.69; H 4.77.
 $C_{11}H_8O_5$. Calculated %: C 59.46; H 4.50.

h) Data on direct titration in aqueous alcohol solution in the presence of phenolphthalein:

Found molecular wt. 227.8.
 $C_{10}H_8O_5 \cdot COOH$. Calculated molecular wt. 222.

i) Determination of methyl group. according to Liben: 0.20 g. o-lactyl-phenyl-glyoxylic acid was dissolved with heating in 5 ml. water, 0.9 g. iodine in 3 ml. 10% aqueous potassium iodide added, and 9 ml. 5% solution of potassium hydroxide added to the hot solution. The mixture was boiled for 15 minutes and then extracted with ether. The ether solution was washed with a hyposulfite solution, water, and dried with sodium sulfate. Distilling off the ether yielded 0.25 g. iodoform of m.p. 118°C. Yield 70%.

j) Preparation of silver salt. 1.0 g. of o-lactyl-phenyl-glyoxylic acid was dissolved in the cold in 10 ml. water and neutralized with 5% aqueous ammonia solution to a weak-alkaline solution with litmus. A small amount of o-lactyl-phenyl-glyoxylic acid was added to the solution until slightly acidic. A few drops of 10% silver nitrate produced a precipitate. The latter was filtered off and another 5 ml. of silver nitrate solution was added to the mother liquor. Cooling the solution separated white crystalline precipitate of the silver salt, which was filtered off and washed first with water, and then with alcohol. Weight 0.5 g.

Found %: Ag. 32.51.
 $C_{11}H_8O_5Ag$. Calculated %: Ag. 32.80.

3. Preparation of esters of o-lactyl-phenyl-glyoxylic acid.

a) 1.0 g. o-lactyl-phenyl-glyoxylic acid, 10 ml. absolute methyl alcohol and 2 drops of concentrated sulfuric acid were boiled on a water bath for 6 hours. The reaction mixture

was dissolved in ether, and the ether solution was washed with a 10% soda solution, then with water, followed by drying with sodium sulfate. Distilling off the ether yielded a syrup which crystallized rapidly. Weight 1.0 g; m.p. 125°C. Two crystallizations from diisooamyl ether with a subsequent washing of the crystals with pentane and drying in vacuo at 50°C at 5mm. yielded methyl ester melting at 132°C.

Found %: C 60.95; H 5.26.
 $C_{12}H_{12}O_5$. Calculated %: C 61.00; H 5.08.

Ethyl ester of o-lactyl-phenyl-glyoxylic acid can be obtained under the same conditions. M.p. 128°C (from diisooamyl ether).

b) 0.5 g. of silver salt of o-lactyl-phenyl-glyoxylic acid and 10 g. of methyl iodide were shaken continuously for 36 hours. The precipitate of silver iodide was filtered off and washed with ether. Distilling off the ether yielded 0.3 g. of a white crystalline substance which was twice recrystallized from diisooamyl ether, and washed on the filter with pentane. The compound melted at 132°C and gave no depression of the melting point in a mixture with the methyl ester obtained in the previous experiment 3a.

4. Reaction of o-lactyl phenyl-glyoxylic acid with o-phenylenediamine

To 10 g. of the former, dissolved with heating in 10 ml. alcohol, was added 1.0 g. of o-phenylenediamine, dissolved in 10 ml. hot water. A yellow precipitate was formed. After boiling for 20 minutes the reaction mixture was cooled, and the precipitate was filtered off. Weight 1.1 g. The compound was recrystallized several times from alcohol. After drying in vacuo at 70°C at 5 mm, it melted at 178°C. The compound is insoluble in hot or cold alkali.

Found % C 69.26; H 4.92; N 9.75.
 $C_{12}H_{10}O_5N_2$. Calculated % C 69.38; H 4.76; N 9.52.

5. Action of alkali on o-lactyl-phenyl-glyoxylic acid in the presence of oxygen from the air.

a, Separation of 2-hydroxy-1,4-naphthoquinone. 0.10 g. substance and 20 ml. 5.5% aqueous potassium hydroxide were placed in a round bottom flask equipped with a reflux condenser and a tube extended to the bottom of the flask and connected with a gasometer. The originally colorless solution turned yellow on boiling, and after passing the first air bubbles from the gasometer turned dark red. After 30 minutes of boiling in a current of air, the solution was cooled, acidified with sulfuric acid, and the yellow precipitate extracted with ether. The ether solution was dried with sodium sulfate, and the ether was distilled off. Yield 0.08 g. m.p. 186-187°C. After recrystallization from methyl alcohol, m.p. 190-191°C. The product gave no depression of the melting point in a mixture with 2-hydroxy-1,4-naphthoquinone and produced readily an anilide described by Liberman [6] (red needles from alcohol m.p. 191-192°C). A mixed sample of this substance with anilide melted at the same temperature. Yield of 2-hydroxy-1,4-naphthoquinone 93%.

b, Determination of split off carbon dioxide. The determination was carried out in a small three-necked flask, fitted with a dropping funnel, tube extended to the bottom of the flask, and with a reflux condenser. The air, introduced from the gasometer into the flask, was purified from carbon dioxide by passing through 3 Tishchenko flasks, containing 40% sodium hydroxide solution and a flask containing water. The air and carbon dioxide passing through the reflux condenser were introduced in a titrated alkaline solution placed in two flasks connected in series. A Tishchenko flask containing 40% sodium hydroxide solution was connected to the end of the system.

0.2106 g. o-lactyl phenyl glyoxylic acid were placed in a three-neck flask. Each of the flasks contained 30 ml. of 0.1 N alkaline solution to absorb carbon dioxide. After checking the system for leaks 40 ml. 5.5% of potassium hydroxide were introduced from the dropping funnel and the passage of air from the gasometer started. The solution was heated to boiling, boiled for 30 minutes, then cooled and acidified with 30% sulfuric acid which was introduced through the same dropping funnel. The solution was heated to boiling and boiled

15 minutes, in a current of air, to completely remove the carbon dioxide formed. Upon completion of the experiment, the solution of alkali used for the absorption of carbon dioxide was back-titrated with 0.1 N acid solution, first to a phenolphthalein end point, and then to a methyl orange end point. 12.49 ml. 0.1 N alkaline solution was used up for the liberated carbon dioxide. In a preliminary experiment it was established that for the carbon dioxide obtained from potassium carbonate present in 40 ml. 5% potassium hydroxide, 3.22 ml. 0.1 N alkaline solution was consumed. Therefore, for the carbon dioxide formed as a result of this reaction, a total of 9.27 ml. 0.1 N alkaline solution were required; calculation showed 0.48 ml. required. Thus, the yield of carbon dioxide was 97.7% of theoretical.

6) Action of alkali on o-lactyl-phenyl-glyoxylic acid in the absence of oxygen.

A small three-necked flask was fitted with a dropping funnel, a tube extending to the bottom of the flask, and a reflux condenser connected with a Tishchenko flask which contained an alkaline solution of pyragallol. The system was filled with hydrogen (or nitrogen) purified by passing through an alkaline solution of permanganate and pyragallol. For a final purification to remove traces of oxygen the hydrogen (nitrogen) was passed through an ignited tube filled with copper. A small safety flask was placed between the inlet tube and the three-necked flask. Into the flask were introduced 20 ml. water, 1.0 g. o-lactyl-phenyl-glyoxylic acid, the system was checked for leaks and the air was displaced by means of hydrogen. To remove the air dissolved in water, the contents of the flask were heated in an atmosphere of hydrogen for 1 hour and, after cooling, 30 ml. of 18% aqueous alkali solution were added from the dropping funnel. The reaction mixture at first turned yellow, and then brown. After boiling for 30 minutes in a current of hydrogen, 12 ml. 50% sulfuric acid was added through the same dropping funnel. A pinkish-gray precipitate of 1,2-naphthohydroquinone-4-carboxylic acid was filtered off. Weight 0.45 g.; m.p. 190-192°C (with decomposition). After two crystallizations from water in the presence of bone black, the decomposition temperature was 194°C. G. Heller obtained this acid by another method and reported the decomposition temperature as 195°C [5].

Found %: C 64.84; H 3.79
 $C_{11}H_8O_4$. Calculated %: C 64.79; H 3.43.

Number of active hydrogen atoms determined by the method of Zerevitinov-Terent'ev 3.19 and 3.03.

Titration of this acid with alkali was only possible in the absence of oxygen from the air; in the presence of the latter a bright red salt of 2-hydroxy-1,4-naphthoquinone was formed, and it was difficult to determine the end point in titration.

The titration was carried out in an atmosphere of hydrogen in an aqueous-alcoholic solution in the presence of phenolphthalein.

Found molecular wt. 208.8 and 210.2.
 $C_{10}H_7O_2$ COOH. Calculated molecular wt. 204.

1,2-naphthohydroquinone-4-carboxylic acid was oxidized by using nitric acid (sp. gr. 1.2) to the corresponding quinone under conditions described by G. Heller [5]. Starting with 0.2 g. of the hydroquinone the yield was 0.16 g. 1,2-naphthoquinone-4-carboxylic acid of m.p. 164-165°C (from glacial acetic acid); Heller reported m.p. 165°C.

Found %: C 65.25; H 3.16.
 $C_{11}H_6O_4$. Calculated %: C 64.34; H 2.97.

The quinone reacts in an alcoholic solution with aniline, forming an anilide - dark red needles of m.p. 260°C; this corresponds to the data reported by G. Heller [5].

7. Action of alkali on 1,2-naphthohydroquinone-4-carboxylic acid in the presence of oxygen from the air.

a) Isolation of 2-hydroxy-1,4-naphthoquinone. The reaction was carried out under

the conditions described for experiment 5a. The isolation of 2-hydroxy 1,4 naphthoquinone was also carried out with the observation of the conditions described in this experiment. Starting with 0.2 g. of naphthohydroquinone-4-carboxylic acid, the yield was 0.18 g. quinone. After washing with small amounts of ether and recrystallization from methyl alcohol this melted at 190-191°C and gave no melting point depression in a mixture with 2-hydroxy-1,4-naphthoquinone. The quinone was also characterized by its conversion to an anilide (m.p. 191°C) and 2-hydroxy-3-nitro-1,4-naphthoquinone (m.p. 157°C). The properties of the compounds were similar to those reported in the literature [8,9].

b) Determination of split-off carbon dioxide. The determination was carried out under exactly the same conditions as described in experiment 5 b.

Weight 0.2104 g. 1,2-naphthohydroquinone-4-carboxylic acid. For carbon dioxide formed during the reaction 7.98 ml. 0.1 N. alkali solution were consumed; whereas the calculated amount was 10.32 ml.. Yield of carbon dioxide: 77.32%.

CONCLUSIONS

It has been shown that the 2-methyl-1,4-naphthoquinone oxide when boiled with water undergoes oxidative-hydrolytic transformations giving rise to phthiocol, 2-methyl-1,4-naphthoquinone, and o-lactyl phenyl glyoxylic acid. This latter compound has been investigated in detail. The process of its oxidation to 2-hydroxy-1,4-naphthoquinone and its principal reactions have been investigated in great detail.

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OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

V. MECHANISM OF OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF 2-METHYL-1,4-NAPHTHOQUINONE OXIDE

L. A. Shchukina and M. M. Shemyakin

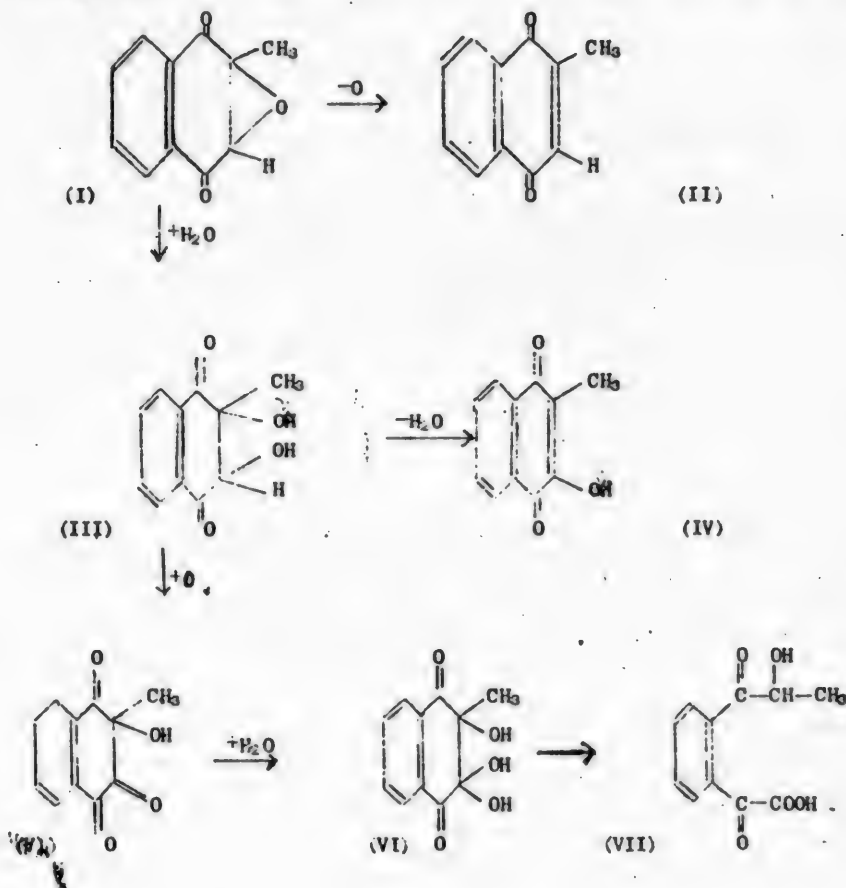
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In studying the influence of the degree of oxidation of quinone molecules on the ease of hydrolytic cleavage of their cyclic groupings, an investigation was made of the conditions and character of the oxidative-hydrolytic cleavage of 2-methyl-1,4-naphthoquinone (I) oxide. In the previous communication [1] it was shown that the cleavage of this oxide could be accomplished readily by boiling it with water. This process did not require the presence of oxygen and resulted in the formation of o-lactyl-phenyl-glyoxylic acid (VII), together with considerable amounts of 2-methyl-3-hydroxy-1,4-naphthoquinone (phthiocol) (IV), and 2-methyl-1,4-naphthoquinone (II). However, the mechanism of the cleavage of the cyclic grouping of the initial oxide and the intermediate steps of the whole process were not clarified and required additional experimental investigation. At the same time the clarification of these questions was necessary for an understanding of the nature of the steps in the oxidative hydrolytic cleavage of quinones and the products of their oxidation. For this reason, a further investigation was undertaken of the mechanism of the cleavage of 2-methyl-1,4-naphthoquinone (I) oxide when boiled with water.

A comparison of the formulas of the initial oxide ($C_{11}H_8O_3$) and of the final o-lactyl-phenyl glyoxylic acid ($C_{12}H_{10}O_6$) indicates that the formation of the latter should be connected not only with the hydrolytic, but also with oxidative transformations, passing through a series of intermediate steps. Since together with the acid phthiocol was always present, it could be assumed that it represented an intermediate product in the conversion of the oxide to o-lactyl-phenyl-glyoxylic acid (VII). However, on the basis of the investigations described in one of the earlier communications [2] this assumption can be rejected. In fact, it was established that phthiocol was incapable of undergoing changes on protracted boiling with water either in the absence or in the presence of oxygen from the air. Apparently, this was the reason for its presence among the transformation products of the initial oxide. However, it was shown that boiling phthiocol with water at pH above 7 caused a purely hydrolytic cleavage to occur. This gave rise, however, not to o-lactyl-phenyl-glyoxylic acid, but to o-propionyl phenyl glyoxylic acid and to the secondary product of its transformations -- 2-methyl indenone 1-carboxylic acid-3. Therefore, o-lactyl-phenyl-glyoxylic acid (VII) is formed from 2-methyl-1,4-naphthoquinone (I) oxide, not through phthiocol (IV); the latter, apparently, represents, not an intermediate but a side product, obtained as a result of hydration followed by dehydration of 2-methyl-1,4-naphthoquinone oxide.

What then is the actual manner of formation of o-lactyl-phenyl-glyoxylic acid? The structure of this acid, the necessity during its formation for the presence of both an oxidiz-

ing and hydrolyzing agent, and also a series of new experimental data, suggest the following scheme:



A detailed examination of the separate steps of this process and those experimental data which may be used to justify the proposed mechanism follows:

1. The formation of the glycol (III) as a first intermediate product follows from the fact that when the oxide (I) was boiled with water, in addition to o-lactyl-phenyl-glyoxylic acid (VII), phthiol (IV) was always formed. It is known that the oxides of quinones and their respective glycols are readily transformed to hydroxy quinones [9-10]. It is obvious that the oxides undergo hydration followed by dehydration; therefore, the formation of phthiol (IV) during the reaction indicates that it was preceded by the formation of glycol (III).

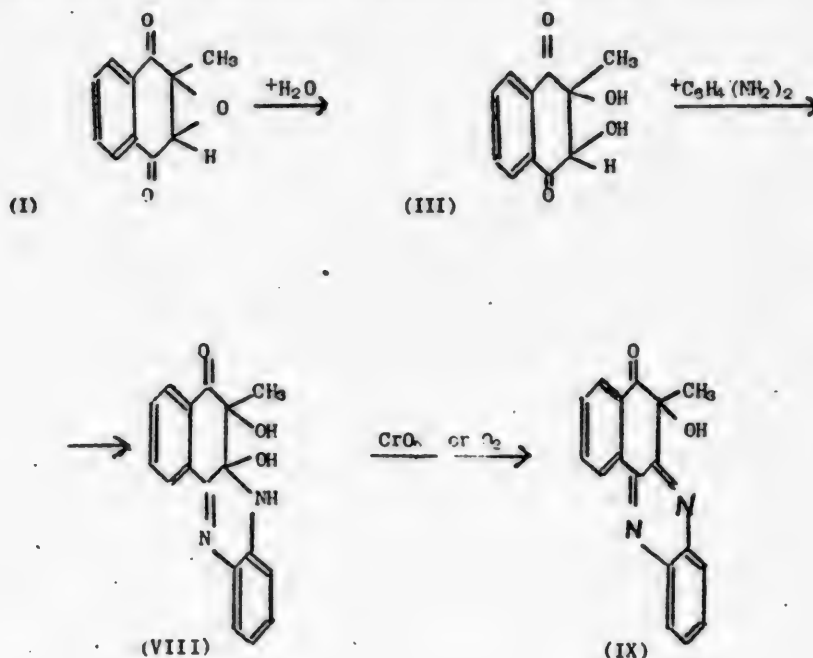
At present the formation of this glycol as a first intermediate product of this process has been fully confirmed by the isolation of the respective azine derivative (VIII) in the reaction of splitting the oxide in the presence of o-phenyldiamine.

The formation of the azine derivative (VIII) started rapidly as soon as the 2-methyl-1,4-naphthoquinone oxide was boiled with water containing dissolved o-phenyldiamine. However the separation of this compound and its purification could be facilitated by carrying out the reaction of a period of 1-1.5 hours. The azine derivative (VIII) formed a precipitate of bright orange crystals. It could be readily obtained in a pure state after several

recrystallizations from benzene. The investigation of this substance confirmed the structure expressed by formula (VIII).

According to analytical data, its composition corresponds to the following formula: $C_{17}H_{14}O_2N_2$. By using the method of Zerevitinov-Terent'ev it was found that the molecule contained two active hydrogen atoms. The characteristic bright-orange coloration of the compound also correlated with structural formula (VIII). This coloration was apparently due to the presence in the molecule of a system consisting of seven conjugated double bonds, having at one end a chromophore (carbonyl group, on the other end an auxochrome (secondary amine group)).

A decisive proof of the structure of the isolated product was provided by its oxidation to an azine derivative (IX); this latter structure was well established (in collaboration with Ya.B.Shvezov) not only by an extensive investigation of its properties but also by synthesis. The process of oxidation could be realized practically in quantitative yield by reacting with chromic anhydride in acetic acid solution.



Thus, there is no doubt that the first stage of the transformation of 2-methyl-1,4-naphthoquinone (I) oxide to the final product o-lactyl-phenyl-glyoxylic acid (VII) is the hydration of this oxide, giving rise to compound (III) as a first intermediate product.

2. An examination of the second step of the process: the formation of an intermediate hydroxytriketone (V) follows.

It was established that when the initial oxide was boiled with water for 7-8 hours in a current of air in the presence of o-phenylenediamine an azine derivative was formed, which corresponded to hydroxytriketone (V). The structure of this compound, expressed by formula (IX) was verified in this laboratory in collaboration with Yu.B.Shvezov (for details - see [1]).

On the other hand it was shown that the azine derivative obtained from compound (III) having the structure (VIII) could be oxidized under the same conditions, i.e., when boiled for a long period of time with water in a current of air, to the same compound (IX).

Thus, the data provided by the experimental work are sufficient to confirm not only the first, but also the second step of the suggested scheme of transformation of 2-methyl-1,4-naphthoquinone oxide (I) to o-lactyl-phenyl-glyoxylic acid (VII).

3. Since it was established that this reaction proceeded through the formation of hydroxyketone(V) as an intermediate product it was essential to provide experimental evidence for the last stage also of the suggested scheme that hydroxyketone was capable under the reaction conditions, i.e. when boiled with water, of undergoing hydrolytic cleavage with the formation of o-lactyl-phenyl-glyoxylic acid (VII). For this purpose, the authors in collaboration with Yu.B.Shvezov, developed methods for the synthesis of this hydroxyketone (and also its acetyl derivative) from the corresponding chloroketone; it was shown that even when heated with water for only a brief time o-lactyl-phenyl-glyoxylic acid (VII) was formed. Thus, the last step of the proposed scheme has been experimentally confirmed.

4. The above data reveal clearly that the process of conversion of 2-methyl-1,4-naphthoquinone oxide (I) to the final product - acid (VII) did not have a purely hydrolytic but had an oxidative-hydrolytic, nature. Naturally, o-lactyl-phenylglyoxylic acid was obtained in this case in a smaller amount.

The ability of 2-methyl-1,4-naphthoquinone oxide to develop oxidative properties has been established by several examples. Thus, it was shown that by observing definite conditions it oxidizes quantitatively monovalent negative iodine to free iodine, and also divalent iron to trivalent, being at the same time reduced to 2-methyl-1,4-naphthoquinone. Therefore, sufficient data exist to regard 2-methyl-1,4-naphthoquinone (II), formed together with o-lactyl-phenyl-glyoxylic acid when 2-methyl-1,4-naphthoquinone oxide is boiled with water, as a reduction product of this acid. It also should be emphasized that when the reaction was conducted in the absence of oxygen from the air the yield of 2-methyl-1,4-naphthoquinone was increased. In this case it can be assumed that 2-methyl-1,4-naphthoquinone was also capable of developing oxidative properties, especially in those cases when the reaction was carried out in solution at a pH above 7 (compare communication II [1]).

It is of interest to observe that the oxidative ability of 2-methyl-1,4-naphthoquinone oxide is not a specific property of this compound alone. Comparatively recently it was shown that some carotenoid oxides also can be reduced to their corresponding carotenoids [12-15].

All these data confirm the proposed scheme for the oxidation-reduction reactions of 2-methyl-1,4-naphthoquinone oxide.

EXPERIMENTAL*

1. Formation of azine derivative (VIII) in the process of oxidative-hydrolytic cleavage of 2-methyl-1,4-naphthoquinone oxide (I).

In a three neck flask provided with a reflux condenser was placed 1.5 l. of distilled water. The water was heated to boiling, followed by introduction of 4.5 g. of o-phenylene diamine and 6 g. of 2-methyl-1,4-naphthoquinone. The solution turned bright red and after 10 minutes a red crystalline precipitate separated. After one hour the hot reaction mixture was filtered off (A small amount of a red crystalline precipitate was also separated from the mother liquor on cooling but it was contaminated with 2-methyl-1,4-naphthoquinone oxide and other admixtures; therefore, it was difficult to purify). The precipitate was removed from the filter and, after being treated with hot water, filtered again and washed repeatedly on the filter with hot water. The weight of the dry material was 4.5 g. The compound was recrystallized three times from benzene by using bone[†] and then dried in vacuo to a constant weight at 85°C and 5 mm. Product: bright orange crystals of m.p. 147°C^{••}.

* The analytical part of the investigation was carried out in collaboration with E. A. Ignat'eva.

•• The same results were obtained when the reaction was carried out in an atmosphere of hydrogen.

Found %: C 73.27, 73.30, 73.57; H 5.29, 5.01, 5.03; N 10.21.
 $C_{17}H_{14}O_2N_2$. Calculated %: C 73.38; H 5.04; N 10.08.

The number of active hydrogen atoms, determined by the method of Zerevitinov -Terent'ev, is 2.05.

The product is insoluble in cold acid and alkali. When heated with acid or alkali it undergoes changes. The product is readily soluble in acetone and ether, and sparingly soluble in alcohol. It is sparingly soluble in cold glacial acetic acid; when heated to boiling it is dissolved with difficulty, developing first a red coloration which, after a few seconds changes to a dark violet precipitate. The latter is insoluble in acetone, benzene and hot glacial acetic acid. It does not melt when heated to 260°C.

2. Oxidation of azine derivative (VIII)

a) 0.5 g. of the substance was dissolved in the cold in 10 ml. glacial acetic acid and to this solution was added 0.2 g. chromic anhydride first dissolved in the cold in 25 ml. glacial acetic acid. The coloration of the reaction mixture changed rapidly from brown-red to gray-green. After 2 minutes the reaction mass was poured into 200 ml. water to which was then added a 20% aqueous alkali solution. This alkaline solution was extracted twice with ether. The ether extract was dried with sodium sulfate and the ether removed. Product - 0.5 g. light yellow substance which, after two recrystallizations from alcohol yielded white crystals of m.p. 188-189°C.

The isolated compound had properties identical with the azine derivative (IX), described in detail in communication VIII [11]. A mixed sample of both substances melted at 188-189°C.

Found %: C 73.79; H 4.44.
 $C_{17}H_{12}O_2N_2$. Calculated %: C 73.91; H 4.34.

Acetylation of the compound under conditions described in communication (VIII) (experiment 26) [11] yielded a substance which after recrystallization from alcohol had a m.p. 213-214°C. It was identical with the acetylated azine derivative (IX), described in communication VIII [11]. A mixed sample of both substances melted also at 213-214°C.

b) In a three neck flask provided with a reflux condenser and tube extending to the bottom of the flask which was used for passing air during the experiment, was introduced 0.5 l. of distilled water. The water was heated to boiling and 1 g. of the azine derivative (VIII) obtained in experiment 1 was introduced. The boiling was continued for 6 hours and the red coloration of the reaction mixture gradually changed to yellow. The precipitate formed on cooling was filtered off. Weight 0.6 g. The mother liquor was extracted twice with ether and the ether solution dried with sodium sulfate. After distilling off the ether, an additional 0.3 g. of a yellow precipitate was obtained which was combined with the precipitate mentioned above and recrystallized twice from alcohol using bone black. Yield 0.4 g. white crystalline compound of m.p. 188-189°C, identical with that obtained in the previous experiment.

3. Formation of an azine derivative (IX) in the process of oxidative-hydrolytic cleavage of 2-methyl-1,4-naphthoquinone oxide.

Into a three neck flask provided with a reflux condenser and a tube extending to the bottom of the flask, through which air was passed during the experiment, was placed 1.5 l. of distilled water. The water was heated to boiling, followed by the introduction of 4.5 o-phenylenediamine and 6 g. 2-methyl-1,4-naphthoquinone oxide. The boiling was continued for 7 hours. The reaction mixture developed a red coloration which gradually changed to yellow brown. Upon completion of boiling, the reaction mixture was cooled and the brownish yellow precipitate was filtered off. Weight of precipitate 4.5 g. Two recrystallizations from alcohol yielded 2 g. of a white crystalline substance of m.p. 188-189°C. The isolated compound had properties identical to those of the azine derivative (IX) described in communication VIII [11]. A mixed sample of both substances melted at 188-189°C.

4. A study of the oxidative properties of 2-methyl-1,4-naphthoquinone oxide.

a) Reaction with potassium iodide. 0.1-0.2 g. of oxide were dissolved in 15 ml. of glacial acetic acid and 0.5 g. of potassium iodide was added to the solution. The reaction mixture was boiled in a flask fitted with a reflux condenser for 15 minutes, then cooled, diluted with 150 ml. of water and the liberated iodine titrated with thiosulfate.

0.1536 g. substance: 16.28 ml. 0.1 N. $\text{Na}_2\text{S}_2\text{O}_3$.
 $\text{C}_{11}\text{H}_8\text{O}_3$. Calculated: 16.55 ml. 0.1 N. $\text{Na}_2\text{S}_2\text{O}_3$.

Upon completion of titration the solution was extracted four times with ether. The ether solution was dried with sodium sulfate, the ether distilled off and the residue dried in vacuo to constant weight. Product: 0.1398 g. of compound (m.p. 105°C), in a mixture with 2-methyl-1,4-naphthoquinone gave no depression in melting point. Yield: 98.3%.

b) Reaction with the sulfate of ferrous oxide. 0.5001 g. of oxide was dissolved in 5 ml. of acetone. To the solution were added 5 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 10 ml. of water, and 3 ml. of concentrated hydrochloric acid. The mixture was boiled in a flask provided with a reflux condenser for 2.5 hours, then the acetone was distilled off and the solution was cooled. The yellow precipitate formed was distilled off. Weight 0.4472 g.; m.p. 104°C. The product, in a mixture with 2-methyl-1,4-naphthoquinone gave no depression of the m.p. Yield - 97.8%.

CONCLUSIONS

A proposed mechanism for the oxidative-hydrolytic cleavage of 2-methyl-1,4-naphthoquinone oxide has been investigated and experimentally confirmed.

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